Controls on the water chemistry of headwater streams: synthesis and regional modelling

Thesis

Controls on the water chemistry of headwater streams: Synthesis and regional modelling.

A thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

by

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Abstract

An understanding of the dominant processes controlling streamwater chemistry is critical for the development of a regional water quality model. The relative importance of a variety of catchment characteristics in determining streamwater chemistry in the English Lake District is investigated in this thesis. Fifty-five streams were sampled on a bimonthly basis over the period May 1996 through March 1997.

Rock samples were analysed using X-ray fluorescence analysis. The major- and trace-element geochemical data was used to classify the suite into six rock types. The geochemical data was also used to establish weathering patterns, which suggested that greywackes and lithic arenites weather the easiest, andesites and dacites exhibit heterogeneous weathering and the metamorphosed slate and granite are the most resistant to weathering.

Forty-one (75%) of the streams can be considered sensitive to acidification on the basis of their alkalinity and thirty-eight (69%) can be considered sensitive to acidification on the basis of their calcium concentrations. Statistical analyses showed that flow-weighted concentrations of alkalinity and base cations were lowest in the catchments with resistant bedrock, thin or peaty soils, at high altitudes or receiving relatively high loads of sulphur and nitrogen deposition.

A multiple regression model incorporating some of these factors provided a fairly good approximation of alkalinity concentrations on a spatial (R^2 value of 56%) and temporal scale (R^2 value of 49%). The predicted alkalinity was within 50 $\mu eq\ l^{-1}$ of the observed (simulated) values for 77% of the sites.

Although the model has a fairly good predictive capability, its spatial and temporal applicability outside the study area is an unknown quantity. To satisfy the needs of policy makers and the hydrological community, the model needs to predict alkalinity with a high degree of accuracy in a variety of study areas. This has not been tested as yet, however, the variables used in the final model are not unique to the Lake District or the 1990's and therefore the model may prove to be an extremely useful tool indeed.

Acknowledgements

I came up with an acronym for doing a Ph.D during my first year (**P**ure **h**ell and **D**rudgery) and I can safely say that the last four years have been the most boring, painful and tedious of my life. I seem to have gone up more blind alleys that I thought was feasible but lo and behold I have finished. And thank f*ck for that is all I can say!!!!!

Many people have helped (or hindered depending upon your point-of-view) in the completion of this thesis over the last four years. First of all, I'd like to thank Nancy Dise, Nigel Harris, Paul Whitehead, Alan Jenkins and Mike Edmunds for setting up and supervising the project (This project was funded by an OU studentship). They have all endured constant pestering and often gross stupidity from me but they all have been there with a smile, a kind word and some useful suggestions. On the specifics of the project, Nancy read and corrected all of my chapters very thoroughly and often reduced me to the verge of tears with the amount of red pen she used (hmmm just thought.....maybe she has got shares in Bic® biros). However, before this sounds too negative I would like to acknowledge her support / ideas and in hindsight I am sure that all the corrections **were** necessary. Thanks also to Alan and Paul for commenting on the thesis and for helping me to learn how to use the MAGIC model, and to Mike for pointing out flaws in my methods at an early stage and helping me comprehend the chemical reactions involved at the water-rock interface. Nigel contributed enormously to my understanding of Lake District geology and helped me grasp the concepts behind geochemical interpretation. At this point I would also like to reserve special thanks for Colin Neal because of his fountain of knowledge, new ideas and general support.

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Mike "Coco the clown" Henty, Mabs Gilmour and Kay Green all helped with advice on sample preparation and lab protocol. John Holbrook also deserves a special mention for controlling the purse strings and making sure that I didn't have to dig into my student overdraft too much! For general cartography advice and constant banter, massive thanks go to Andy Lloyd (for being fat and Welsh) and John Taylor (for being a fellow slaphead). Dick Carlton also deserves a mention for computing advice as well as his sense of humour. I'm sure I've probably missed someone out so cheers anyway.

Now to the mates section ⇒ The following people have all made life tolerable in the pit of despair that is Milton Keynes – Wrighty, 'camp' Vinny, Houghy, Sim, Anna, Super Cooper, 'no knickers' Dickers, Beth, Louise, Louisa, Blando, Smithy, Bucko, Lloydy, JT, Taff and Lee Oliver. Georg (aka Jurgen the German), Jane and Gav (aka filthy hippy) were cool housemates, and Glyn, Nicky and Jacko were great office mates. Thanks also go to members of the OU and Belgrave St Peters cricket teams and Olney Rugby Club for being friends and teammates (and obviously for the beers and curries afterwards!).

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Now to the personal (some might say slushy) stuff. Jen has been my girlfriend for the past 2½ years and sometimes I wonder what I have done to deserve such a wonderful, beautiful and sexy woman (get yer sick buckets out!). She has been all a girlfriend should be – a best friend, a lover and a shoulder to cry on. The last year has been difficult for me (writing up, temper tantrums, not playing enough sport etc) and her (hassle from kids / husband, divorce problems etc) but I would very much like to take this opportunity to say thanks for everything. Jen, I love you very much. However, I must reserve the biggest thanks for my Mum. She has been a constant support (financial and emotional) throughout my life and I wouldn't be where I am today without her help. Thanks Mum – if I end up half the person you are, I'll have done well.

As a final word I would like to dedicate this thesis to my Nan, who died before I got the chance to say goodbye, I love and miss you Nan.

Dedicated to the memory of Phyllis May Hardyman (RIP)

Preface

The Lake District is the largest national park in England. Its range of geologies and land use make it ideal for a stream monitoring programme looking at acidification. Built-up areas are kept to a minimum in National Parks and thus human modification to streamwater chemistry in the form of point pollution from urban areas is minimal. Human influence is primarily through land use changes and diffuse pollution via atmospheric sulphur and nitrogen.

Objectives

The objective of this thesis is to understand further the dominant processes in controlling streamwater chemistry and to create a simple regional predictive water quality model.

Thesis Layout

Chapter One is the literature review. It sets the scene by defining 'natural' water chemistry and details how opinions changed during the 'acid rain debate'. It then tackles the catchment parameters thought to be primarily responsible for controlling streamwater chemistry. Also reviewed are a variety of empirical and process-based models.

Chapter Two describes the study area and presents details of the field and laboratory protocols. It also discusses the underlying principles and assumption of multiple regression analyses, principal component analyses and the process-based model, MAGIC.

Chapter Three is a description of the geological history of the study area. It presents the geochemical data gathered during this study and assesses how these new observations relate to previous studies. It also presents a method for deriving rock sample weathering patterns using critical element ratios.

Chapter Four is an interpretation of the catchment characteristic and streamwater data. This can be sub-divided into (i) major-ion chemistry during the six surveys and relationships with geology, land use and soils; (ii) flow-weighted chemistry and relationships with geology, land use, soil and atmospheric deposition; (iii) using geochemical data as an aid for investigating catchment contributions; and (iv) using space as a surrogate for time to assess the effects of land use conversion and/or climate change. It also presents the geochemical data gathered during this study and assesses how these new observations relate to previous studies.

Chapter Five uses a variety of approaches in an attempt to create a simple regional predictive water quality model. It assesses the usefulness of multiple regression and principal component analyses for explaining variations in streamwater chemistry. It also uses the process-based model, MAGIC, to determine catchment weathering rates.

Chapter Six summarizes the results from the whole thesis. It examines the weaknesses of the research and suggests a few future research directions.

Publication of results

The research described in this thesis has been reported in one published abstract and four published papers and these are referenced within.

Thornton, GJP, Dise, NB, Whitehead, PG, Jenkins, A & Edmunds, WM. (1997) Alkalinity and nitrate concentrations of streams in the English Lake District (Cumbria). *Journal of Conference Abstracts 2(2)* p312

Thornton, GJP & Dise, NB. (1997) Major-ion chemistry of streams draining the English Lake District (Cumbria). *Proceedings of the BHS 6th National Symposium, University of Salford.* p2:17-2:24.

Thornton, GJP (1998) Chemical composition of the streams draining the English Lake District: Relationships between stream chemistry and catchment characteristics. *In: Headwaters: Water Resources and Soil Conservation (Eds MJ Haigh, J Krecek, GS Rajwar & MP Kilmartin), AA Balkema: Rotterdam: Brookfield,* p97-109.

Thornton, GJP & Dise, NB. (1998) The sensitivity of streams to acid deposition in the English Lake District (Cumbria): The role of catchment characteristics. *Hydrology of a Changing Environment. Volume I, (Eds H Wheater & CJ Kirby), John Wiley & Sons, London,* p547-558.

Thornton, GJP & Dise, NB. (1998) The influence of catchment characteristics, agricultural activities and atmospheric deposition on the chemistry of small streams in the English Lake District. *The Science of the Total Environment Vol 216 (1),* p63-75.

It is expected that results from the thesis will produce a further two / three papers in due course. A description of how these might be structured can be found below.

1. The geochemical data and weathering patterns derived in Chapter Three are worthy of publication. The geochemical data itself does not reveal anything new about Lake District geological processes, but the weathering patterns aspect is a new and interesting approach and may be suitable for publication in a *Yorkshire Geological Society Special Publication.*
2. Chapter Five relates to the creation of a predictive water quality model. This is the main thrust of this thesis and would be suited for submission to *Water, Air and Soil Pollution* or *Environmental pollution.*
3. Appendix G presents MAGIC applications of each catchment. By compiling and condensing the data, running some forecast predictions and adding some interpretation of the data would make it suitable for submission. It would be suited for submission to *Hydrology & Earth Systems Science* or *Science of the Total Environment.*

Chapter 1 Background

Chapter 2 Methods

Chapter 3 Whole-rock chemistry of Lake District catchments

Chapter 4 Major-ion chemistry of Lake District streams in relation to catchment characteristics

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CHAPTER 1

Background

"THESIS, n. A short research article padded. A species of composition bearing the same relation to science that the panorama bears to art."
- 'The Devils Dictionary' by Ambrose Bierce

1.1. Importance of headwater streams and human impacts on their chemistry

Water is probably the most precious resource on Earth. Water flowing over and through the earth is crucial to almost all the environmental processes. In addition, an adequate, unpolluted water resource is fundamental to human survival and the key to economic development. It is easy to argue that the war to maintain water fit for human consumption is growing increasingly harder due to declining supplies (brought about by the higher demand from the rising populations) and increasing pollution (due to global industrialisation). Much of the public concern over water pollution incidents has been associated with this threat to the potable water supply and consequently research has tended to concentrate on freshwater lakes, reservoirs and/or sizeable streams in close proximity to urban areas. Research carried out includes problems with cyanobacterial blooms (Howard *et al.*, 1995, 1996a,b; Howard, 1997; Kneale and Howard, 1997), heavy metal pollution (Salkauskas, 1998; Schreck, 1998) and dumping toxic waste (Anon, 1997), and are primarily concerned with the implications for consumptive purposes.

The water bodies used in the above research are generally large and located in lowlands. For this reason their chemistry is the result of many processes, both "natural" and anthropogenic, and it is hard to distinguish the relative role that each process plays in determining water chemistry. It is therefore preferable to limit the amount of "noise" in the chemical signal by studying headwater streams. Headwater streams are found in the upper parts of the river drainage system often originating at the source of the river, whereas streams lower down the system integrate many different streams and sub-catchments. Studying headwater streams, which are frequently relatively pristine single stream catchments, allows us to understand the governing processes in streams more fully, and subsequently allows us to examine the influence that anthropogenic processes exert on the "natural" stream chemistry.

1.1.1. "Natural" headwater stream chemistry

The solute chemistry of a stream is dependent on the many processes that occur within its catchment. Precipitation itself has very low concentrations of dissolved solids, but chemical reactions with the catchment result in stream water with larger ionic concentrations. Some chemical constituents exported into the stream system, most noticeably silica (SiO_2) and calcium (Ca^{2+}), are principally products of weathering (White *et al.*, 1971). Other ions, such as chloride (Cl^-) and sulphate (SO_4^{2-}), are generally deposited into the catchment from the atmosphere.

Over time, the ion concentration of a stream may fluctuate widely for several reasons, including variations in discharge and seasonal influences. In addition, concentration differences may arise from the variation in sampling regimes and analytical techniques (Harned *et al.*, 1981). These may result in observed differences rather than real differences, thus masking the actual trends that are occurring in the water bodies. For example, during stormflow conditions, large amounts of base-deficient rainwater may be mixed with base-rich groundwater causing flushes of acidic water or "acid episodes" (UKAWRG, 1988; Wigington *et al.*, 1990; Davies *et al.*, 1992). This changing hydrological regime results in changing sensitivity over time to stresses, such as acidification by acid deposition (Section 1.1.2), or eutrophication by excess nitrogen. It also means that spot samples of streamwater chemistry may vary greatly over the period of 1 year. Water must be analysed over different hydrologic and seasonal conditions, therefore, to integrate this variability.

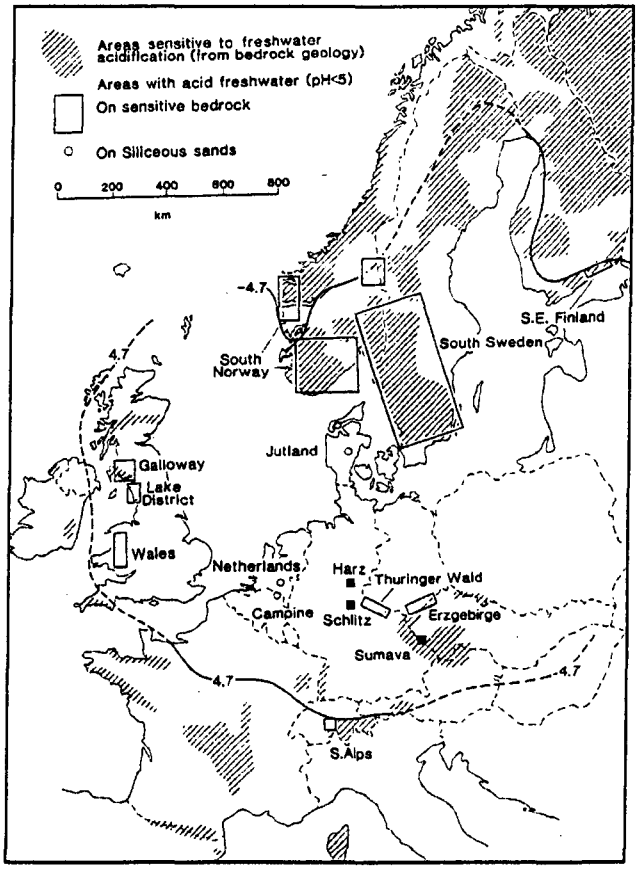
The water chemistry of a stream reflects the prevailing weathering processes, drainage pathways and residence times of the catchment. When exposed to anthropogenic stresses, this chemical signature can change, as discussed Sections 1.1.2 and 1.1.3.

1.1.2. Acidification

A dictionary definition of an acid is 'any substance that dissociates in water to yield a corrosive solution containing hydrogen ions' (Uvarov and Isaacs, 1986), whereas acidification is 'the increase of hydrogen ions at the expense of base cations (i.e. calcium, magnesium, sodium and potassium) in the terrestrial or freshwater environment' (Uvarov and Isaacs, 1986). These simplistic definitions give no indication of the processes that control acidification, any insight into why certain areas become acidified while others do not and whether it is a natural or 'man-made' problem.

Acidification is a natural process that occurs in soils and water (Reuss *et al.*, 1987) and air pollution is not a new phenomenon. However, the acidification of natural surface waters in upland areas is a recent development to an old problem and significant areas of Europe are 'under threat' (Figure 1.1). The recent acceleration in the rate of acidification of soils and freshwater has led to increased media interest and much scientific endeavour.

Figure 1.1 - A map showing areas in Europe where acidification is a problem



Emission of sulphur (S) and nitrogen (N), which are acidifying compounds, into the atmosphere occurs from a wide variety of sources. These compounds are chemically altered in the atmosphere prior to being deposited (Section 1.1.2.a). Once deposited as dry or aqueous media, the compounds are subsequently modified by an interaction with vegetation, soils and geology. It is this modification at the interface between water and geology (Section 1.2.1), soils (Section 1.2.2) and vegetation / land use (Section 1.2.3) which determines the surfacewater chemistry of catchments. The factors that most influence

catchment sensitivity to surfacewater acidification will need to be represented in the predictive model (Chapter 5).

Aluminium and pH were traditionally used for the biological 'tolerance ranges' of plants and animals to stresses such as acidification. However, a growing number of researchers employ calcium and alkalinity as sensitivity indicators because they reflect both the physical and the biological 'health' of a system. Many researchers use 200 $\mu eq\ l^{-1}$ as the upper limit of the sensitivity threshold (cf. Altschuller and McBean, 1979; Hendrey *et al.*, 1980; Haines *et al.*, 1983; Linthurst, 1983), thus allowing the watershed to be classified as sensitive (or non-sensitive) to acidification via acid deposition.

a. Acid precipitation

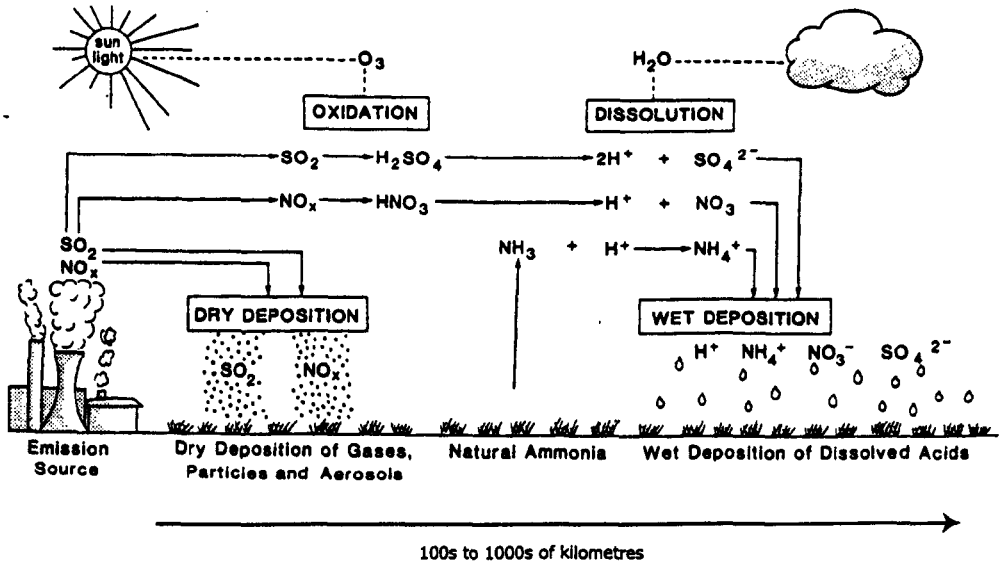
'Acid rain' is not a recent, or anthropogenically induced, development. In equilibrium, the pH of 'clean' rain is 5.67 (Park, 1987), due to naturally occurring acids and bases and carbonic acid (H_2CO_3) - formed by atmospheric reactions with carbon dioxide (CO_2). Acid deposition brings an increase in the input of strong acid anions into stream catchments and background rainfall pH values varied between 4.6 and 5.6 at pre-industrial European sites, mainly due to variations in the sulphur cycle (Galloway *et al.*, 1982).

As early as 1852, Robert Angus Smith (an English chemist) coined the phrase "acid rain" when discussing the chemistry of rain in Manchester. In the 19th Century, air pollution was fairly localised as acid rain was restricted to cities and natural streams and lakes far from the city were not affected. People, however, were severely affected by the acrid air and, as populations grew, pollution increased to intolerable levels. Smith's early work on the chemical climatology of cities (Smith, 1872) was largely ignored until his ideas inspired further pollution research by a Canadian ecologist, Eville Gorham. Gorham carried out detailed research on the rainwater chemistry of the Lake District in the 1950's (Gorham, 1955). Later he suggested that many of the soils in Northern England and Scotland were acidic due to anthropogenic air pollution, or more specifically the acidification of air masses as they passed over the large industrial centres (Gorham, 1958).

Problems with the acrid urban atmosphere came to a head when an estimated 4000 people died during the London pea-souper between 5-9th December 1952 (Royal-College-of-Physicians, 1970). The technological advances of the 1950's and 1960's produced a solution to this urban pollution problem: build tall chimneys. These tall chimneys improved local air quality enormously by transporting sulphur and nitrogen into the regional atmospheric circulation belts. The "out of sight, out of mind" attitude amongst policy-makers led to the approach that "dilution was the solution to pollution" (Park, 1987). However, the pollutants

simply didn't disappear, they were simply deposited as sulphuric and nitric acids hundreds of miles from the source (Figure 1.2).

Figure 1.2 - Simple representation of the chemistry and dispersion of acid precipitation



A decade later it was argued that 'acid rain' was killing fish in Sweden and that the origins of the polluted precipitation were the heavily industrialised parts of Britain, USA and western Europe (Oden, 1968). Svente Oden, a Swedish soil scientist often regarded as the father of acid rain studies, was the first to recognise the problem of international trans-boundary acid rain and began a campaign in the early 1970's to inform the scientific community about acid rain and its assumed causes. The widespread interest amongst politicians and scientists, as well as the general public meant acid rain was no longer a scientific curiosity but a matter of international diplomacy (Park, 1987). Indeed, the British Labour government confessed in the mid-1970's that sulphur dioxide from British power station chimneys was beginning to be deposited over Norway and much of Scandinavia. However, claims by Scandinavian scientists during the 1980's, that air pollutants from Britain and the USA were responsible for acidified precipitation in Scandinavia were largely ignored under the Thatcher and Reagan administrations. At this time, the British and American governments were not convinced that costly remedial measures required to reduce emissions would produce the desired effect, hence the British government refused to

ratify the proposed EEC directive to reduce emissions by 60%. It was not until the late 1980's and early 1990's that they accepted that long-range air pollution, resulting from Britain's power stations, was a concept that had arisen from their newly acquired ability to exploit the global-scale refuse depositories.

b. Natural vs anthropogenic acidification

Much of the concern over acidification has centred on soils (Sverdrup *et al.*, 1994; Zech *et al.*, 1994; Gower *et al.*, 1995), freshwaters (Mason, 1990; Caritat, 1995) and its consequent effects on aquatic life (including Overrein *et al.*, 1980; Rahel and Magnusson, 1983; UKAWRG, 1988; Henriksen *et al.*, 1989; Carline *et al.*, 1992). However, not every acidic water body or soil is the result of anthropogenic pollution. Natural soil acidification occurs when organic acids and carbon dioxide are produced during the decomposition of plant remains (Catt, 1985), or when base cations are leached because precipitation exceeds evapotranspiration (Brady, 1990). In addition, as organic acids build up in the surface layer the soil becomes colonised by acidophilic plants (e.g. *Sphagnum* and *Calluna vulgaris*) which break down and form an even more acidic soil (Cresser and Edwards, 1987). Natural freshwater acidification occurs when the catchment bedrock is resistant to weathering and the soils are thin and sandy (Patrick *et al.*, 1981), or when there is a large accumulation of peat (Langan and Wilson, 1992). Naturally occurring acidic streams have been known since the late nineteenth century (Stokes, 1884), but many 'pristine' streams have become more acidic in the latter half of the twentieth century due to acid deposition. By examining records detailing water quality change, we should be able to distinguish which freshwater bodies have been artificially acidified and which are naturally acidic. Yet, in reality, the paucity of historical data in headwater areas makes any assessment of temporal water quality decline very difficult. In the next section, some of the evidence of water and soil acidification is discussed (Section 1.1.2c).

c. Evidence of acidification

A few records of catchment geochemistry do exist for soils and streams in the UK. For example, one study compared the chemistry of Welsh upland streams between the 1960's and mid-1980's (Ormerod and Edwards, 1985). It concluded that the pH of moorland streams had an average decline of 0.7 pH units between the 1960's and 1980's, whilst afforested streams had an average pH decline of 1.7 pH units. The authors suggested that increased acidification in the forested areas had occurred due to the trees scavenging acidic compounds from the atmosphere. In another study, the soil pHs in north-east Scotland were

compared between 1949 and 1987 (Billett *et al.*, 1990). This study found that the pH of soils had declined by 0.5 pH units over this time period and the cation exchange capacity (CEC) had also fallen considerably. The authors suggested that the decrease in pH (and the associated decline in CEC) were linked to soil acidification brought about by air pollution.

Using historical studies in this manner causes problems because the analytical and sampling methods often vary, thus preventing accurate comparisons. The lack of long-term monitoring networks means that other methods are required for evaluating changes in water quality. The lack of study data and the ensuing interpretation problems in many areas means that palaeolimnology is used as an alternative evaluation of water quality decline.

Two British palaeolimnologists, Roger Flower and Rick Battarbee, came up with a fairly simple and accurate method for assessing changes in water chemistry over long time scales. They used the species composition of diatom assemblages present in lake sediment to reconstruct the historical pH of the lake (Flower and Battarbee, 1983). They suggested that by dating each sediment layer (using ^{210}Pb), counting the diatom taxa and observing changes between acid-tolerant (e.g. *Tabellaria spp*) and acid-sensitive taxa (e.g. *Fragilaria spp*) in the diatom assemblage, can construct a pH curve within ± 0.25 pH units.

The relationship that Flower and Battarbee developed between diatom assemblages and pH has since been used to infer the history of acidification at many lakes in Europe and North America. The timing of acidification inferred by this method varies from less than a decade, to more than 150 years ago. For example, studies in the Galloway, Scotland, have suggested a decline in lake pH of 0.5 to 1.5 pH units since the mid-1800s (e.g. Battarbee *et al.*, 1985, 1989; Flower *et al.*, 1990) with the most rapid decline occurring in the post-war period due, it is hypothesised, to significant pollutant deposition (Kreiser *et al.*, 1990). However, some lakes in this region have not yet been acidified and one (Loch Fleet) only became acidified in 1975 (Anderson *et al.*, 1986). Elsewhere in the UK, Cumbrian lakes and tarns apparently have not acidified further between 1928 and 1980 (Sutcliffe *et al.*, 1982; Haworth *et al.*, 1987) and several Welsh lakes have experienced a pH decline of 0.5 pH units since 1930 (Flower *et al.*, 1994). Outside of the UK, at least half of 50 Finnish lakes studied have shown clear signs of acidification in the 20th century and most have suffered a pH decline of 1.1 to 1.5 units since 1960 (Merilainen and Huttunen, 1990). Other diatom studies have also shown a rapid decline in pH since 1950 at other Scandinavian lakes (Renberg and Hellberg, 1982), as well as at lakes in the USA (Harter, 1988).

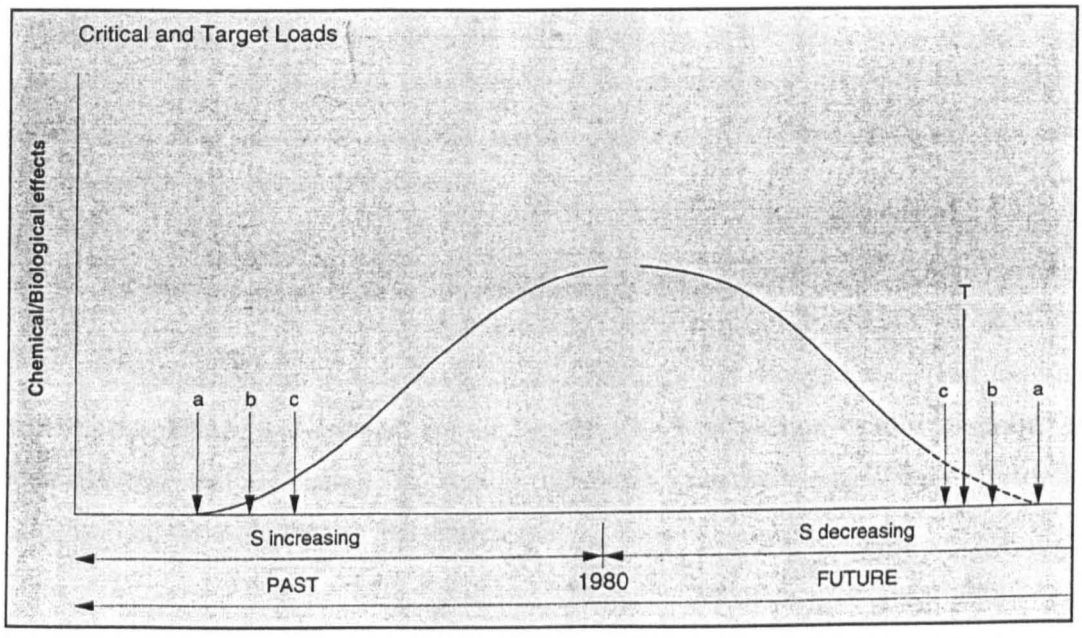
d. The Critical Loads concept

Critical loads have been defined in many ways, but the most commonly used definition is that of Nilsson and Grennfelt (1988):

> *'A critical load for acid deposition is the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function.'*

European and UNECE countries have embraced the critical load concept as a basis for setting their emissions policies by using critical load exceedance maps and target loads for the country in question. This concept is best illustrated by Figure 1.3 where the chemical or biological effect is related to an increased acid loading over time (often called a dose-response relationship).

Figure 1.3 - Critical and target loads concept diagram



In Figure 1.3, the critical load for the site is exceeded at point **a** on the left-hand side of the diagram (points **b** and **c** represent the critical loads of different species at that site), and as acid deposition decreases in the future a target load, **T**, is chosen to protect a particular species, or to enable full recovery (points **a**, **b** and **c** on the right side of the diagram).

e. The acidification debate

The role of acid deposition in the recent acidification of upland freshwater and soils, was vigorously debated in the 1980s (Park, 1987). At the centre of the debate was the relative importance of deposited anthropogenic acids and natural organic acids in causing acidification. Many researcher suggested that the effects of acid deposition were minor compared to natural sources of acidity (for example, Rosenquist, 1978; Krug and Frink, 1983), whereas much of the research has shown a strong relationship between acid deposition and acidification (for example, Overrein *et al.*, 1980; vanBreemen *et al.*, 1984).

Earlier in this Chapter, the relative roles of acid rain (Section 1.1.2a) and 'natural' acidity (Section 1.1.2b) as causes of soil and water acidification were discussed. However, probably the most logical explanation was provided by Reuss *et al* (1987), who suggested that much of the acidification of soils and water is caused by acid deposition being superimposed upon natural acid production.

The response of a stream to chronic deposition of nitrates, sulphates and acidity varies considerably depending upon the soils, geology, morphology and land use of the catchment. Thus, the chemical composition of the streamwater reflects a wide range of processes in the catchment and the relative importance of each of these catchment characteristics is discussed in Section 1.2.

1.1.3. Ramifications of changes in streamwater chemistry

Acidification has a wide range of ramifications for the freshwater and terrestrial ecosystems, which are summed up in Figure 1.4. This section briefly describes the repercussions that a change in stream chemistry, or more specifically freshwater acidification, can have for fish and aquatic life.

a. Fish

It is thought that streamwater pH in the range 6.5 to 9.0 is required to support large fish populations (Alabaster *et al.*, 1988). However, it is also quite possible that streams below pH 6.5 will support fish whilst some streams with pH above 6.5 will be fishless. However, the broad guidelines for the effects of different streamwater pH on fish populations can be found in Table 1.1.

Figure 1.4 - Environmental impacts of acidification

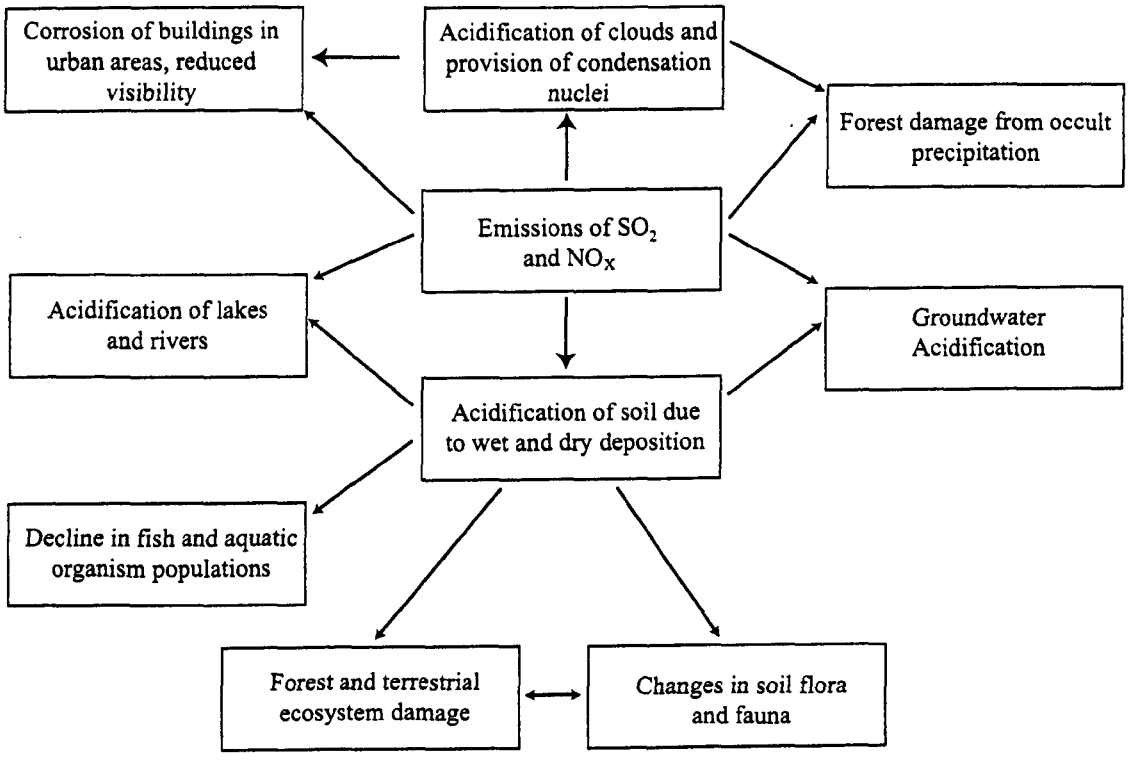


Table 1.1 - The effect of streamwater pH on fish population, survival and reproduction
(Source: European Inland Fisheries Advisory Committee, 1969)

Streamwater pH	Effect on fish
11.5 – 11.0	Lethal to fish
11.0 – 10.0	Some roach and salmon survive
10.0 – 9.0	Harmful to fish
9.0 – 6.5	Normal (Harmless to fish)
6.5 – 6.0	Reduction in fish reproduction
6.0 – 5.0	Small fish populations (High Al = Toxicity)
5.0 – 4.5	Harmful to most fish eggs
4.5 – 4.0	Harmful to fish (Only pike can breed)
4.0 – 3.5	Roach, tench and pike survive. Salmon mortality
3.5 – 3.0	Toxic to all fish (Some invertebrates may survive)

In the UK, many studies have detailed the decline in salmon (*Salmo salar*) populations due to recent freshwater acidification. For example, despite supporting large salmon populations in the 1950s, many acidic upland streams in Cumbria have become

'fishless' in the last two decades (Prigg, 1983). Much of the loss is not due to actual fish kills, which require a low streamwater pH (between 3.0 and 4.0), but a lack of reproduction. In a healthy population, there are large numbers in the 'recruitment class' as most of the natural loss occurs in this early stage (Alabaster *et al.*, 1988), but in acidified streams, natural loss often wipes out the annual population because numbers in the recruitment class are much lower (Harvey, 1975).

b. Aquatic life

There is no question that fisheries (a major economic resource) are detrimentally affected by acidification, but there are also concerns about other aquatic life, more specifically how the change in certain 'key' species can have a knock-on effect for the whole ecosystem through foodwebs and competition (Jeffries and Mills, 1990). The broad guidelines for the effects of different streamwater pH on aquatic organism populations can be found in Table 1.2.

Table 1.2 - The effect of streamwater pH on aquatic organisms
(Source: Department of Energy and Environment, 1978)

Streamwater pH	Effect on aquatic life
8.0 – 6.0	Normal conditions. Decrease of 0.5 to 1.0 pH unit will result in changing community composition. Some species will be eliminated.
6.0 – 5.5	Reproduction in species number and ability to withstand stress.
5.5 – 5.0	Reduction in the diversity of species. Some species eliminated (e.g. molluscs, zooplankton, phytoplankton, amphipods) Several pH tolerant species dominate
5.0 – 4.5	Decomposition of detritus is severely impaired. Most species eliminated.
< 4.5	Exacerbation of all above effects. Lower algal limit

The flora and fauna of acid waters are typically less diverse than circumneutral waters. In the UK, several studies have detailed the decline in invertebrate (e.g. mayfly, stonefly, mollusc, crustacean) and macrophyte (e.g. sphagnum, lobelia) populations and diversity due to recent freshwater acidification. For example, in Cumbrian streams, much of the reduction in invertebrate diversity (Sutcliffe and Carrick, 1973a) is a knock-on effect of the population decline in certain macrophyte species (Sutcliffe and Carrick, 1986).

1.2. Controls of surface water chemistry

Whether acid deposition leads to acidified waters depends upon the level of buffering in the catchment. A stream's sensitivity to acidification is primarily controlled by a number of factors including the soil, geology and land use of the catchment. The chemical composition of the streamwater reflects not only deposition, but also a wide range of processes in the catchment. The relative importance of each of these catchment attributes is discussed in the following sections.

1.2.1. Bedrock

The buffering capacity of a particular lithology stems from the amount of carbonate and weatherable silicate minerals present (Bricker, 1986). Other influences on the amount of weathering include: the amount of exposed surface (White, 1995), the structure of the rock (i.e. does it have large fractures or joints, cf. Stallard, 1995) and the residence time of the catchment (i.e. longer residence time usually results in more weathering, cf. Drever and Clow, 1995).

The weathering rate from bedrock and soils is of paramount importance for the catchment's ability to buffer incoming acid precipitation. However, weathering rates are particularly difficult to measure and apply at the catchment scale (Paces, 1986). There are several approaches for determining catchment weathering rates including (a) simple mass balance (Garrels and Mackenzie, 1967); (b) laboratory experiments (Schnoor, 1990); (c) biogeochemical models (Sverdrup and Warvfinge, 1995); and (d) indicator elements (White and Blum, 1995). This thesis utilises two of these approaches to infer the role of geology in streamwater chemistry (Chapter 4 – indicator elements) and to determine catchment weathering rates (Chapter 5 – biogeochemical models).

Indicator elements

By extending the mass balance approach, this approach focuses on elements that are presumed to have limited interaction with other ecosystem processes, such as sodium and silica. After determining the mineralogy of a rock, the stoichiometric ratio for each of the key elements can be determined by solving a series of linear equations (representing weathering reactions).

For sodium, once the stoichiometry of weathering is known, then the fluxes of the other cations can be calculated by multiplying the sodium flux by the appropriate stoichiometric ratio. However, there are several problems with this method. For example, in

low weathering coastal zones, the flux of sodium from weathering is comparatively small in relation to the sea-salt input, and in areas of human activity, the input from road salt and fertiliser make the method unworkable (Drever and Clow, 1995). Silica is often used as an alternative.

Silica can be established with more certainty than sodium because the input of silica is small from the atmosphere and very large from weathering processes (Paces, 1986). However, silica is retained in different ratios by secondary minerals and thus weathering rates may vary hugely depending on the type of secondary phase. For example:

Albite to gibbsite ⟶ ratio of albite to silica is 1:3

$$H^+ + NaAlSi_3O_8 + 7H_2O \longrightarrow Al(OH)_3 + Na^+ + 3H_4SiO_4$$

Albite to kaolinite ⟶ ratio of albite to silica is 1:2

$$H^+ + NaAlSi_3O_8 + 4.5H_2O \longrightarrow 0.5\ Al_2Si_2O_5(OH)_4 + Na^+ + 2H_4SiO_4$$

Thus, silica flux is not a simple direct indicator of the weathering rate of primary minerals.

Biogeochemical models

The majority of biogeochemical computer models are developed to simulate the processes governing watershed biogeochemistry to a high level of accuracy and complexity. However, the complexity of weathering rate simulation varies widely. Process-orientated models (e.g. PROFILE – Sverdrup and Warfvinge, 1988) consider weathering in terms of the reactions involved for individual mineral equilibria, whereas lumped parameter models (e.g. MAGIC – Cosby *et al.*, 1984) generally only simulate weathering rates as a catchment specific release of base cations or ANC.

Detailed data on the mineralogy of individual soils was not available for this project, therefore, PROFILE could not be used. This thesis uses the lumped parameter model, MAGIC, to optimise catchment weathering rates. The underlying principles involved in the calculation of weathering rates within MAGIC are fully discussed in Section 2.5.2 and by Cosby *et al* (1984), and the results can be found in Chapter 5 and Appendix G.

1.2.2. Soils

Soils are principally derived from the breakdown of the underlying bedrock. Other soil-forming factors, which contribute heavily to the 'make-up' of upper and surface

horizons of the soil, include the breakdown of plant / animal matter and microbial activity. Base cations, like calcium and magnesium, may be released (weathering) or retained (cation exchange) by the soil. In addition, acid anions, like sulphate, may be retained (adsorption) by the soil. The buffering capacity of a particular soil stems from the amount of weathering, cation exchange and sulphate adsorption that occurs (Brady, 1990). As bedrock and soil weathering are inextricably linked, the importance of weathering is not covered here as it was previously discussed in Section 1.2.1. Cation exchange (one of the most crucial processes in determining the composition of streamwater) and sulphate adsorption are discussed below.

Cation Exchange

Clay minerals, an important consequence of weathering, and decayed organic matter, a product of decomposition, have the important property of adsorbing cations on their negatively charged surfaces. Presented in its simplest form, the adsorbed cation on the soil colloid (e.g. calcium) is replaced by (exchanged with) two hydrogen ions from the soil solution thus having a neutralising effect on the solution. Once all the exchange sites have been used by hydrogen ions, the hydrogen ions entering the soil will remain in solution and contribute to surfacewater acidification.

The cation exchange capacity (CEC) is the sum total of exchangeable cations that the clay minerals and organic matter in the soil can adsorb (retain). The base saturation of the soil is the proportion of exchange sites that are occupied by basic exchangeable cations (i.e. cations other than hydrogen and aluminium), which include calcium, magnesium, sodium, potassium and ammonia. Base saturation is expressed as a percentage of the total CEC.

Sulphate adsorption

Retention of sulphate in soils is thought to be an important factor in determining the effects of acid deposition on streamwater (Reuss *et al.*, 1986). Some soils can adsorb sulphate on the positive surfaces of iron or manganese oxides. The mobile anion concept (Johnson and Cole, 1980) suggests that sulphate is removed from soil solution in the same manner as hydrogen during cation exchange thus mobilising base cations into solution. However, once sulphate adsorption capacity is exceeded, sulphate remains in solution and contributes to surfacewater acidification.

Acid deposition mainly impacts the surface layer and upper horizons of the soil, whereas weathering and cation exchange generally are more important in the deeper soil horizons. A detailed review of the response of soils to acid deposition is not presented here but there is an extensive amount of literature covering this topic (for example, Reuss and Johnson, 1985; Cresser *et al.*, 1986; Eriksson *et al.*, 1992; Mulder and Cresser, 1994).

1.2.3. Land Use

The chemical signature imparted to a stream by the bedrock and soil may be modified or obscured by land use practices (Bricker and Rice, 1989). In the UK, land management strategies are particularly important for altering soil chemistry (Hornung *et al.*, 1986) and deposition efficiency (Fowler *et al.*, 1989). The two most important management strategies employed in UK uplands, conifer plantations and agricultural liming, are discussed below.

Conifer plantations

A number of authors have found that freshwater acidification increases following the onset of large-scale conifer plantations (for example, Neal *et al.*, 1986; Ormerod *et al.*, 1989; Waters and Jenkins, 1992; Harriman *et al.*, 1994). This has also been supported by evidence of a change in historical lake pH (using diatom assemblages to reconstruct the pH history – cf. the method of Flower and Battarbee, 1983) after the planting of the conifer forest (Kreiser *et al.*, 1990).

The increase in water and soil acidity in catchments affected by conifer plantations could be due to any or all of the following reasons: (i) reduction of base cations in soils due to uptake by trees (Hornung, 1985); (ii) scavenging of acidic atmospheric compounds by trees (Neal *et al.*, 1992c); (iii) less (but more concentrated) runoff because of evapotranspiration (Bird *et al.*, 1990); and (iv) removal of base cations from the system by clearfelling / harvesting (Neal *et al.*, 1992b).

Agricultural liming

The application of lime is by far the most widespread management strategy to overcome the natural acidity of upland soils (Ormerod and Edwards, 1985). The application of lime causes an increase in calcium and a reduction in aluminium in the exchangeable cation complex (Hornung *et al.*, 1986) and thus reduces the sensitivity of the soil to acidification (Driscoll *et al.*, 1989). Consequently, agricultural liming was often used to ameliorate the effects of surfacewater acidification (Crawshaw and Diamond, 1988).

1.3 Modelling surface water chemistry

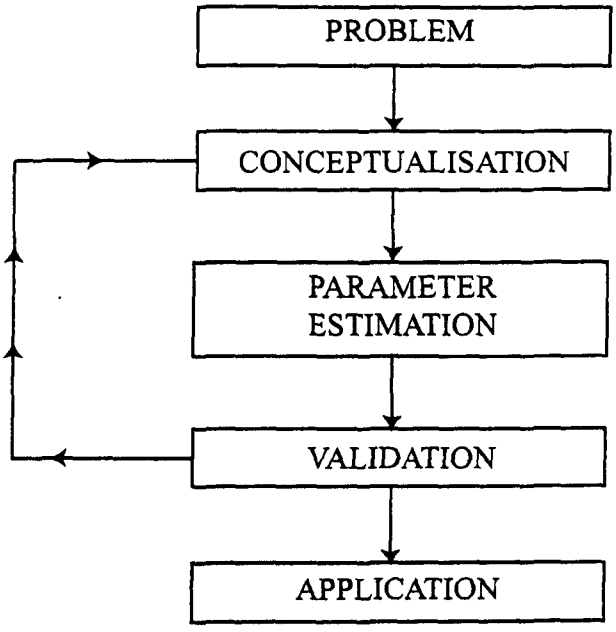
The use of models in science is a widespread phenomenon. Models are constructed by a variety of disciplines including mathematics, physics, chemistry, biology and geology, either in a descriptive or predictive capacity. In the present study field, models are constructed for a variety of reasons. The multidisciplinary nature of the present study field means fieldwork is expensive and complex and this is a major reason for the implementation of models. However, models can also be used to test hypotheses generated by field research or to predict a system's response to change (e.g. decrease in acid rain) and are also often utilised to aid the understanding of processes occurring within the catchment (i.e. conceptual models of watershed function). Although models are a valuable resource it must be noted that models are a vast oversimplification of reality and often the inherent uncertainty of the processes involved in an individual area result in a spatial and temporal aggregation of results. Pre-existing models of acidification were originally developed to satisfy different objectives in different geographic regions (Booty *et al.*, 1992; Eshleman *et al.*, 1995), therefore, the model results often only reflect the differences in process formulations and model complexity.

This section begins with a general introduction discussing the processes and considerations involved in developing a model (Section 1.3.1). It then moves onto a discussion of the various empirical models and their associated literature (Section 1.3.2). The section concludes with a discussion of the various process-based models and their associated literature (Section 1.3.3).

1.3.1. Modelling: A question of scale?

The scale of approach is a very important consideration when creating a model, or even when deciding which model to adopt. There are three initial stages that need to be considered before a model is constructed or chosen. Firstly, the question that requires answering needs to be defined (i.e. what you are trying to achieve with the model). Secondly, the selection of a suitable scale to answer the question (i.e. catchment, regional or national scale). Thirdly, the type of model needs to be decided upon (i.e. the model that best answers the questions with the resources available). Once the type of model has been ascertained by the three initial stages, the building of a model requires a further four stages which can be found in Figure 1.5.

Figure 1.5 - Four stages of the model building process



The first stage of model building is conceptualisation. In this stage, the relevant variables are selected, ideas about how variables change and interact are formulated, and the model structure is established. The second stage is parameter estimation. In this stage it is necessary to assign numerical values to some unknown constants. It also involves the process of selecting the model data that most accurately reproduces the "real" data (i.e. calibration). The third stage is validation. It is necessary to check whether the model reproduces observations not used in the calibration and identification stage. If the model does not accurately reproduce the data it is necessary to go back to the conceptualisation phase and modify the model. The examination of model stability and sensitivity may result in many model modifications before the fourth stage of application is entered. If the model passes the validation stage, then it may be applied. However, to some extent the model structure and hypothesis are based on the application (i.e. post-hoc hypothesis testing).

There are two main types of model utilised in the study field, simple empirical models and dynamic process-based models. A discussion of the uses and the limitations and advantages of each model type is fully discussed in the following sections (Section 1.3.2 and 1.3.3).

1.3.2. Empirical models

Within the surface water quality literature, there are five main types of empirical model that have been widely utilised: (i) mass-balance models, (ii) ion-balance (or titration) models, (iii) mixing models, (iv) time-series models, and (v) multiple linear regression models.

a. Mass balance models

Mass-balance models have mainly been used to estimate catchment weathering rates (Garrels and Mackenzie, 1967; Langan *et al.*, 1996). Much of the research into the rate of base cation release has been formulated with the impact of acid deposition in mind. Mass-balance models of weathering rates have been utilised to estimate the degree of acidification in watersheds and to develop a dose-response relationship (see Figure 1.3) for freshwaters using critical loads (Henriksen *et al.*, 1986; Henriksen, 1988; Battarbee *et al.*, 1993). It is possible to estimate the weathering rate using a simple mass-balance calculation of the input and output of cations. The major source of inputs into a catchment is atmospheric deposition and outputs are generally in the form of solutes in streamwater. Therefore, by calculating the difference between the atmospherically derived base cations and those in the stream outflow gives the average catchment weathering rate.

Mass-balance models are extremely useful in the field of catchment biogeochemistry, but they do have limitations. Mass-balance models assume steady state conditions (i.e. do not vary in time). There are a number of short-lived processes (e.g. variability in precipitation inputs) that occur in catchments that may cause perturbations in the input-output budget. Therefore, the timescale used in the calculation of the mass-balance is an important consideration. The errors due to transient shifts within the system are reduced significantly by increasing the timescale over which the mass-balance is calculated. Also an accurate quantification of inputs and outputs is crucial if an accurate prediction of the weathering rate is required.

b. Ion balance (Titration) models

Ion balance or Titration models are used to estimate the degree of acidification in watersheds and to predict future changes in acidity. Most of these models are derived from the Henriksen nomograph (Henriksen, 1979, 1980). The nomograph is a consequence of electroneutrality and carbonic weathering reactions. Henriksen likened the acidification of Scandinavian lakes to the titration of a bicarbonate solution with strong acid. A catchment

was considered to be similar to a solution in a beaker - strong acids (from anthropogenic atmospheric deposition) titrate the existing alkalinity of the solution (or replace bicarbonate as the major weathering ion). Simply defined, the Acid Neutralising Capacity (ANC) of a stream is reduced by the incoming acid deposition when the sulphate in deposition replaces the bicarbonate in the stream. However, in addition to increases in sulphate, calcium and magnesium concentrations will change due to an interaction with the vegetation, soils and bedrock. The concept of the 'F' factor was introduced to combat this problem (Henriksen, 1982). The 'F' factor estimates the part of base cation flux resulting from soil acidification and is derived from historical data (Henriksen *et al.*, 1992). The Steady State Water Chemistry (SSWC) model (Henriksen *et al.*, 1986) is a further development of the concept used to calculate critical loads. By setting a critical ANC threshold, based on biota change or damage, a critical load is calculated relating to deposition values required to maintain water chemistry above the critical threshold (Henriksen *et al.*, 1992). The SSWC is based on the principle that excess base cation production should always equal or be greater than acidic anion input. The 'F' factor is not important in pristine environments, but it is the most useful when considering areas with high acid deposition levels (Henriksen, 1995).

Ion Balance models and their subsequent developments are particularly useful in the surface water acidification field but they have a number of assumptions. Alkalinity was estimated from calcium and magnesium which implies that the other base cations have a negligible contribution or are regionally constant (Kramer and Tessier, 1982). Background sulphate concentrations have been ignored or assumed constant suggesting that terrestrial sources of sulphur or sulphate sinks (i.e. biological reduction or soil adsorption) are unimportant (Rogalla *et al.*, 1986). The empirical link between present day water chemistry and deposition flux gives no indication of the timing of recovery in response to declining acid deposition (Jenkins *et al.*, 1997) and neglects the short-term buffering processes that delay acidification and subsequent recovery (Reuss and Johnson, 1985). Despite these inherent assumptions, the ion-balance principle and the 'F' factor used by Henriksen and other subsequent researchers helps the understanding of the processes involved and the likely consequence of altering acid deposition levels to catchments (Reuss *et al.*, 1986).

c. *Mixing models*

Mixing Models are based on the concept that streamwater is a mixture of 'old' water (i.e. soil water) and 'new water' (i.e. precipitation), which has led to their widespread usage in examining episodic acidification. A two-component mixing model was developed to predict the response of streams to episodic acidification (Eshleman, 1988; Eshleman *et al.*,

1995). The conceptual origin (based on the principles of electroneutrality) and the simplicity of parameter estimation (i.e. low data requirements) make the model particularly useful for regional prediction and extrapolation of episodic acidification (Eshleman *et al.*, 1992). The major limitations are the model's assumptions. The model assumes that: (1) ANC is conservative during hydrological events; (2) ANC in the two components is constant over time; and (3) the relative components can be determined using a hydrograph separation technique. Evidence of substantial temporal variability in hydrological events (Hooper and Shoemaker, 1986), buffering by short-term soil processes (Reuss and Johnson, 1985), and the fact that average inflow concentrations cannot be used in hydrograph separation (Kennedy *et al.*, 1986) severely limit the model's accuracy in low data availability areas.

End-Member Mixing Analysis (EMMA) was developed to relate changes in streamwater chemistry to observations of soil-water chemistry (Christophersen *et al.*, 1990; Hooper *et al.*, 1990), and is a development on previous soil water work (Neal and Christophersen, 1989). The model attempts to use soil water "end-members" to explain stream water chemistry. It is suggested that the chemical variation in the water chemistry is a result of the changing proportional contribution of the end-members to the stream. Hooper *et al* (1990) found that three end-members explained the variation in streamwater chemistry: (1) groundwater from the floodplain; (2) groundwater from the base of the hillslope in the upper catchment; and (3) soil water collected 10cm below the surface (i.e. 'A' horizon). The model assumes that the soil solutions have more extreme concentrations than the stream water. Therefore, EMMA results in a triangular plot based on the analysis of the three end-members that should encompass the majority of streamwater observations. The major limitation of the model is the paucity of good soil solution and groundwater chemistry data. Although studies at Panola Mountain Research Watershed, Georgia, USA indicate that the majority of streamwater samples fall within the assigned triangles (Hooper *et al.*, 1990, 1998), work in Norway and Wales suggests that observed soil water end-members are insufficient to explain streamwater chemistry (Christophersen *et al.*, 1990).

d. Time-series models

Time-series models are suitable for water quality studies where the overall input-output behaviour of a system is of prime importance, and where the processes driving the system are particularly complex (Whitehead *et al.*, 1986). The major limitation of time-series models is the sampling frequency. A regular sampling regime (i.e. weekly) may not be adequate for catchments with a fast response time and poor time-series reproductions will result. Therefore, when using time-series models the reproduction of catchment behaviour

grows progressively worse as the sampling frequency decreases. Whitehead *et al* (1986) was able to explain 93%, 65% and 66% of the variation in observed H^+ concentrations against flow at Loch Dee, Scotland (hourly sampling), Birkenes, Norway (daily sampling) and Plynlimon, Wales (weekly sampling) respectively.

e. Multiple linear regression models

Multiple linear regression models evaluate the strength and direction of the relationships between several independent variables and one dependent variable. Lynch and Dise (1985) found that bedrock offered a 95% explanation (i.e. R^2 of 0.95) for streamwater alkalinity in the Shenandoah National Park, USA. They also found that the streamwater alkalinity of sites outside the original study area but underlain by the same geology could be predicted with a fair degree (within 50 $\mu eq\ l^{-1}$) of accuracy. In contrast, Kernan (1996) found that using 39 catchment variables (not all significant) in a multiple regression model could only explain 91% of the variation in alkalinity. After concluding that the concept of the 'best' regression equation from an automatic selection procedure was a fallacy, he undertook regression analyses with a variety of catchment attributes selected with *a priori* knowledge. These results were better, as the 'best' significant equation offered an explanation of 75% (R^2 of 0.75) using only five (2 geology, 2 soil and 1 land use) predictor variables.

Some multiple linear regression models have explored the concept that streamwater chemistry is largely a function of bedrock (for example, Webb, 1984; Lynch and Dise, 1985). In contrast, other models have suggested that streamwater chemistry requires soil, geology and land use factors for accurate predictions (for example, Turk and Adams, 1983; Kernan, 1996). Nevertheless, regression models based on regional or catchment data are an important method of empirical modelling. When used in a predictive capacity, any application to conditions other than those from which the model was developed must be made with caution, as causality is not established. Therefore, perhaps the major role of multiple linear regression models is to highlight significant relationships between variables, thus allowing hypotheses about the governing processes of streamwater chemistry to be generated.

This section has given a brief description of the variety of empirical models generally used in the field of water quality modelling. This is by no means a comprehensive account, but their importance in the context of thesis does not warrant a fuller or more

detailed review. In the next section, some of the process-based models are presented (Section 1.3.3).

1.3.3. Process-based models

Within the acidification literature, there are four process-based models that have been widely utilised: (1) The Integrated Lake-Watershed Study (ILWAS) model; (2) Birkenes model; (3) PROFILE and/or SAFE (dynamic version of PROFILE) model; and (4) MAGIC model.

a. ILWAS model

The Integrated Lake Watershed Acidification Study (ILWAS) model was based on the observations from an integrated study of surfacewater acidification in the Adirondack region, USA (Chen *et al.*, 1983). The model consists of two parts: (i) a hydrological part, which simulates interception, throughfall, evapotranspiration, snow accumulation and melt, freezing / thawing of soil and soil/surface water hydraulics; and (ii) a chemical part, which simulates the concentrations of major cations and anions, monomeric aluminium, organic acids and dissolved organic carbon. Within the model, there are many submodels which consider a wide variety of catchment processes including: deposition, canopy interactions, cation exchange, sulphate adsorption, ion balance and carbonate equilibria, plant respiration, nutrient uptake, nitrification, hydrological and soil characteristics and in-lake processes (Goldstein *et al.*, 1985). However, the inclusion of almost all the 'known' catchment processes has made the model excessively complex and therefore finding sufficiently detailed datasets to drive the model is problematic.

The model applications outside the development area (i.e. Adirondack region) have met with varying success. For example, the model reproduced the observed concentrations and seasonal dynamics of water chemistry very accurately at two experimental sub-catchments in the Risdalsheia watershed, Norway (Eary *et al.*, 1994). In contrast, Booty *et al* (1992) found that there was very poor agreement between the model predictions and observed streamwater chemistry at Batchawana Lake, Canada (r of 0.29 to 0.48).

b. Birkenes model

The Birkenes model was originally developed to describe acidified streamwater chemistry in the Birkenes catchment, Norway (Christophersen *et al.*, 1982). The streamwater chemistry is highly flow dependent, with high flow associated with low pH and calcium and

low flow associated with high pH and calcium. In simple terms, it is a two compartment model representing cation exchange in the upper compartment and weathering processes in the lower compartment. A submodel calculates sulphate concentrations, which is based on the mobile anion concept (Seip, 1980) However, the exclusion of a mass balance equation for exchangeable cations limits the model to short-term (daily to seasonal) applications.

In spite of its limitations, the model has been useful for explaining the change in water quality over short-term episodes. For example, the model's application was fairly successful at identifying important trends in the observed streamwater chemistry at sites in Norway (Christophersen *et al.*, 1984), Canada (Seip *et al.*, 1986) and Sweden (Fleischer *et al.*, 1993). However, the success of predicting observed streamwater values varied enormously from site to site (Reuss *et al.*, 1986).

c. PROFILE / SAFE model

The PROFILE model was originally developed to predict the chemistry and critical loads of soils at Gardsjon, Sweden (intensively studied catchments) using theoretical equations of silicate mineral weathering (Sverdrup and Warfvinge, 1988). PROFILE is a multi-layered steady-state model that considers the conditions in the final state directly with no consideration to the conditions pertaining in the pre- and post-acidification states (Warfvinge and Sverdrup, 1992). Within the model, there are a wide variety of catchment processes considered including: deposition, vegetation uptake of base cations, nitrate and ammonia, nitrification, chemical weathering rate of soil using mineralogy, texture and equilibria reactions of the carbonate system. A thorough description of the model structure (i.e. mass balance equations, kinetic equations and assumptions) can be found in Sverdrup and Warfvinge (1988) and Warfvinge and Sverdrup (1992). A dynamic version of PROFILE has also been developed, SAFE (Warfvinge and Sverdrup, 1991).

The model applications outside the development area (i.e. Gardsjon) have usually produced good agreement between predicted weathering rates and weathering rates from laboratory and budget studies. These include sites in Sweden (Warfvinge *et al.*, 1993; Sverdrup *et al.*, 1994), Norway (Jonsson *et al.*, 1995), Scotland (Hodson *et al.*, 1996; Langan *et al.*, 1996) and Wales (Langan *et al.*, 1996). Therefore, the model is a useful alternative method of measuring weathering rates in catchment soils.

Accurate and reliable estimates of weathering rates are one of the important parameters required to calculate critical loads (Kernan, 1996). Warfvinge and Sverdrup (1992) calculated the critical load in two Swedish catchments and found that PROFILE provided an accurate indication of the different ecosystems' sensitivity to acidification.

However, concerns have been raised about the accuracy of PROFILE weathering rates at the most sensitive sites where the most damage is likely to occur (Jonsson *et al.*, 1995). They found that the uncertainty range between PROFILE weathering rates and observed values in damaged forest soils was ± 40%. In addition, Hodson *et al* (1996) found that PROFILE weathering rates (and critical loads) varied by over an order of magnitude in sensitive sites when the default model values were used in the absence of actual data.

d. MAGIC model

The Model of Acidification of Groundwater In Catchments (MAGIC) model was originally developed to predict the effects of acid deposition on surface- and ground-water chemistry in an intensively studied catchment (White Oak Run) in the Shenandoah National Park, USA (Cosby *et al.*, 1984). MAGIC is an extension of the Reuss-Johnson model, but also includes a sulphate submodel and estimates base cation weathering rates. The model has been widely applied across the globe (see application section below) and is suitable for long-term predictions of a stream's response to changes in sulphur input (see deposition forecast section below) and/or land use (see land use forecast section below). A full description of the model structure (i.e. equilibrium equations, definitions and assumptions) can be found in Section 2.5.2, Appendix D and in Cosby *et al* (1984).

Application

The MAGIC model has been previously applied to a number of catchments in countries around the world including Brazil (Neal *et al.*, 1992a; Forti *et al.*, 1995), Finland (LePisto *et al.*, 1988), Norway (Wright and Cosby, 1987; Wright *et al.*, 1990; Cosby *et al.*, 1995), USA (Cosby *et al.*, 1985a,b, 1986b; Norton *et al.*, 1992; Sullivan *et al.*, 1992), Scotland (Cosby *et al.*, 1986a, 1990; Neal *et al.*, 1986; Jenkins *et al.*, 1988; Wright *et al.*, 1994), Wales (Whitehead *et al.*, 1988a, 1990; Jenkins *et al.*, 1990b; Robson *et al.*, 1991) and England (Whitehead *et al.*, 1993, 1997; Barlow, 1994). In addition, MAGIC 'retrodictions' have been compared with reconstructed pH histories of lakes (using palaeolimnology) with a high degree of success (Cosby *et al.*, 1986a; Jenkins *et al.*, 1990a; Sullivan *et al.*, 1992).

Deposition forecast

Many streams have suffered from progressive acidification. Obviously, constant sulphur emissions at present-day levels would only lead to further acidification of freshwater ecosystems. MAGIC has been applied to predict the water chemistry under a variety of deposition scenarios and to estimate the level of emission abatement required for streams to

recover to their pre-acidification state. A reduction in sulphur emissions of 30 % resulted in a slowing down of decline but no recovery (Jenkins *et al.*, 1990b; Robson *et al.*, 1991; Whitehead *et al.*, 1993, 1997); a reduction of 50% in sulphur emissions resulted in marginal recovery (Cosby *et al.*, 1985a, 1986a; Whitehead *et al.*, 1988a,b, 1990; Jenkins *et al.*, 1990b; Barlow, 1994) and a reduction of 60 to 90% in sulphur emissions resulted in moderate recovery but not to pre-acidification state (Jenkins *et al.*, 1990b; Robson *et al.*, 1991; Whitehead *et al.*, 1993, 1997; Barlow, 1994).

Land Use forecast

Conifer afforestation and harvesting plays an important role in streamwater chemistry (Section 1.2.3). MAGIC has been applied on many occasions to predict the water chemistry under afforestation and deforestation scenarios to assess the impact on surfacewater chemistry (or more specifically acidification). Afforestation has generally led to an increase in streamwater acidification (Whitehead and Neal, 1987), whereas deforestation had led to a reduction in streamwater acidification (Neal *et al.*, 1986, 1992a; Whitehead and Neal, 1987; Forti *et al.*, 1995).

This section has given a brief description of the variety of process-base acidification models but it is by no means a comprehensive account. This thesis uses MAGIC to optimise catchment weathering rates and to 'retrodict' base saturation levels, therefore the context of this thesis does not warrant a fuller or more detailed review.

CHAPTER 2

Methods

"The wind howled. The storm cracked on the mountains. Lightning prodded the crags like an old man trying to get an elusive pip out of his false teeth ..... and the thunder rolled."
- Excerpt from 'Maskerade" by Terry Pratchett

2.1. Introduction

This chapter begins with an introduction to the study area (Section 2.2) which includes a brief discussion of the upland environment (Section 2.2.1), an overview of the area's geology (Section 2.2.2), soils (Section 2.2.3), land use (Section 2.2.4), and atmospheric deposition (Section 2.2.5), and a short look at recent changes in land use and atmospheric deposition brought about by human influences (Section 2.2.6). In addition, the reasoning behind the choice of study sites is discussed in Section 2.2.7.

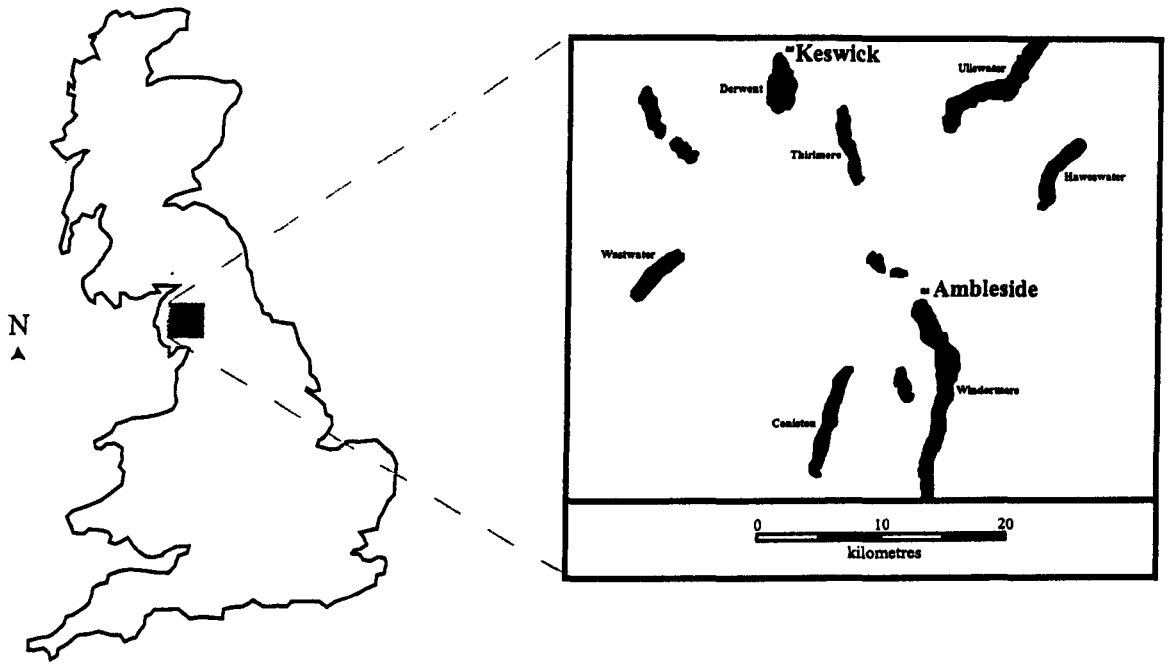
The protocol for the collection of streamwater and rock samples as well as for field measurements is outlined in Section 2.3. In addition, the methods used in the laboratory to analyse the streamwater samples (Section 2.4.1) and rock samples (Section 2.4.2) are also summarised. A fuller description of the analytical techniques used in the laboratory can be found in Appendix B.

The streamwater and rock geochemical data were examined using the statistical methods of multiple regression and principal component analysis, and by the process-based model MAGIC. The chapter concludes with a brief discussion of the principles, underlying structure and assumptions of multiple regression (Section 2.5.1a), principal components analysis (Section 2.5.1b) and the MAGIC model (Section 2.5.2).

2.2. Study Area – The English Lake District

The Lake District is situated in the north-west of England (Figure 2.1), and has a landscape shaped by glaciations with significant areas of high relief (altitudes up to 975 m above sea level). The annual rainfall ranges between 1000–4000 mm depending upon altitude, distance from the sea and geographic location (i.e. windward or leeward side of mountain), and the mean monthly average temperature ranges between 4–15°C at low altitudes, but is significantly colder at higher altitudes.

Figure 2.1 - A map showing the geographic position of the Lake District



Interest in the effects of acid deposition on water quality has engendered many river and lake sampling programmes in the UK (for example, Neal et al, 1990; Edwards *et al.*, 1990; Lees *et al.*, 1990; Mason, 1990; NRA, 1992b). However, until this project was formulated there had been no systematic acidification survey of the streams draining the Lake District. Although some work has been undertaken on the water chemistry of Lake District streams and tarns – for example, Sutcliffe and Carrick (1973a,b,c; 1983a,b; 1988), Sutcliffe *et al* (1982), and Carrick and Sutcliffe (1982; 1983) – but none of these studies were specifically designed with acid deposition in mind. Therefore, this survey was initiated to (a) provide data on the current status of streams in the Lake District, (b) identify the major processes acting on stream watersheds and seasonal variation in water quality, and (c) provide data for the construction of empirical models of the effects of geology, land use, soil and deposition on surface water quality.

2.2.1. The Upland Environment

Upland areas constitute more than a third of Britain's total land area. The upland areas of the U.K. support low populations, possess little heavy industry and are not viable for intensive agricultural use (Countryside-Commission, 1978). Ecologically speaking, they

are often designated (and subsequently protected) as National Parks or Sites of Special Scientific Interest (SSSI's).

In the UK, over 70% of uplands are covered by unimproved native grassland or rough grazing (which includes extensive areas of bare rock), forestry accounts for a further 15%, and the remainder is improved land and urban areas. Despite their small agricultural value, uplands are considered invaluable resources because of their "pristine" nature. For example, the paucity of populated urban areas and intensive agriculture makes them attractive for leisure, such as fishing, hill walking and mountaineering, as well as providing an important resource for the potable water supply. However, uplands can also provide ideal environments for the forestry and agriculture industries who plant widespread conifer plantations and subsidise sheep farming (Parry *et al.*, 1982; Nature-Conservancy-Council, 1987), and this often has severe implications for streamwater quality of the region (Nisbet, 1990; Cannell and Cape, 1991; Hornung and Adamson, 1991; NRA, 1992a).

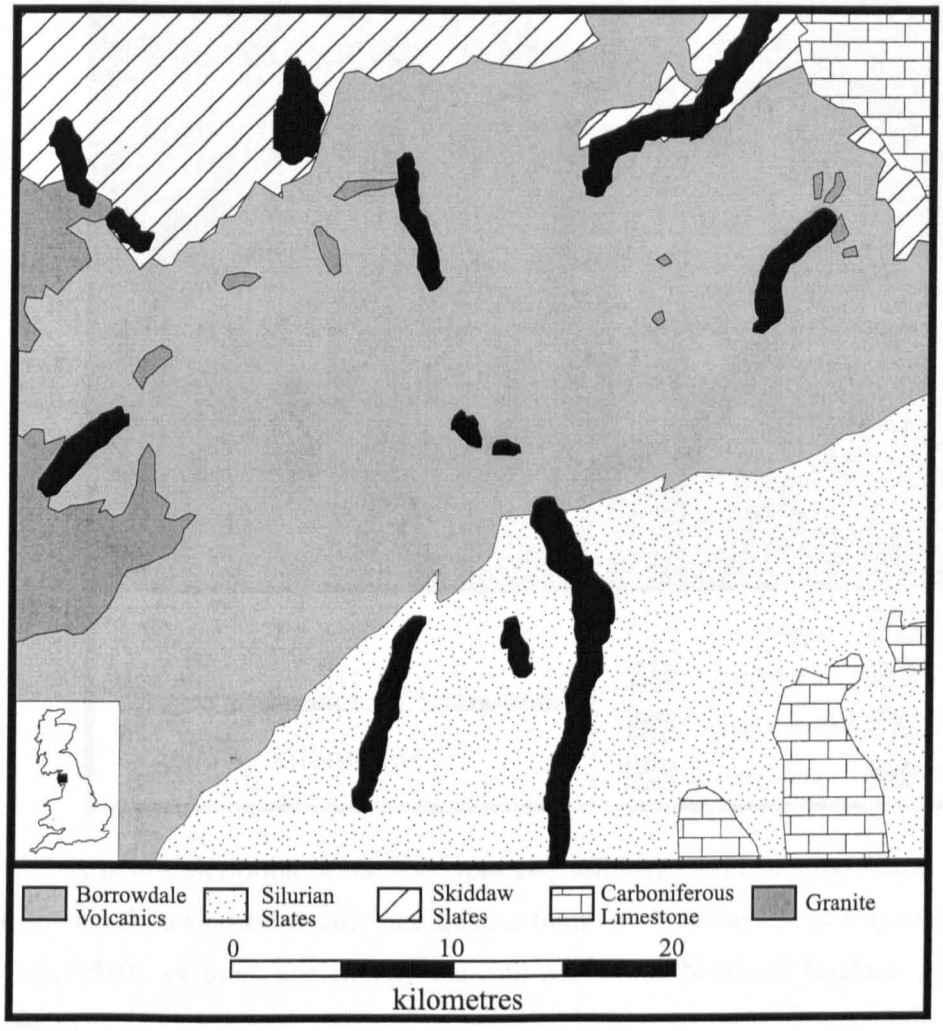
2.2.2. Geology

The geology of the study area is only briefly discussed here. A full discussion of the geological history, geochemistry and classification of the area takes place in Chapter 3.

The central portion of the Lake District consists of three major lithological types trending south-west to north-east (Figure 2.2). The Lake District lithology is further characterised by significant areas of igneous intrusions (Firman, 1978). The Skiddaw Slates, in the north, are the oldest rocks, forming a roughly triangular mountainous zone. The group forms smooth hills comprised of metamorphosed mudstones, flags, grits and shales (Jackson, 1978). The Borrowdale Volcanic Group, Ordovician in age, forms the central core of rugged, craggy hills comprised of very hard lavas and pyroclastic eruptions. This slow-weathering rock group includes a range of extrusive acidic (rhyolites) and basic (andesites) lavas, with volcanic products ranging from fine-grained tuffs (ash) to coarse agglomerates (Millward *et al.*, 1978; Millward and Lawrence, 1985). The Silurian Slates, in the south, are collectively known as the "Windermere Group". These younger sedimentary rocks form the more easily-weathered low-lying hills of the Lake District. They consist primarily of flags, grits, greywackes, mudstones and shales (Ingham *et al.*, 1978). The communication network (roads etc) was easier to set up in the low, rolling landscape than the steep, craggy landscape of the surrounding area, therefore the majority of agriculture and human development is located on the Silurian Slates. The area's topography is dominated by disruptions caused by recent Pleistocene glaciations, which may result in small areas of surficial deposits, such as till and alluvium, having a different provenance to those

deposited locally.

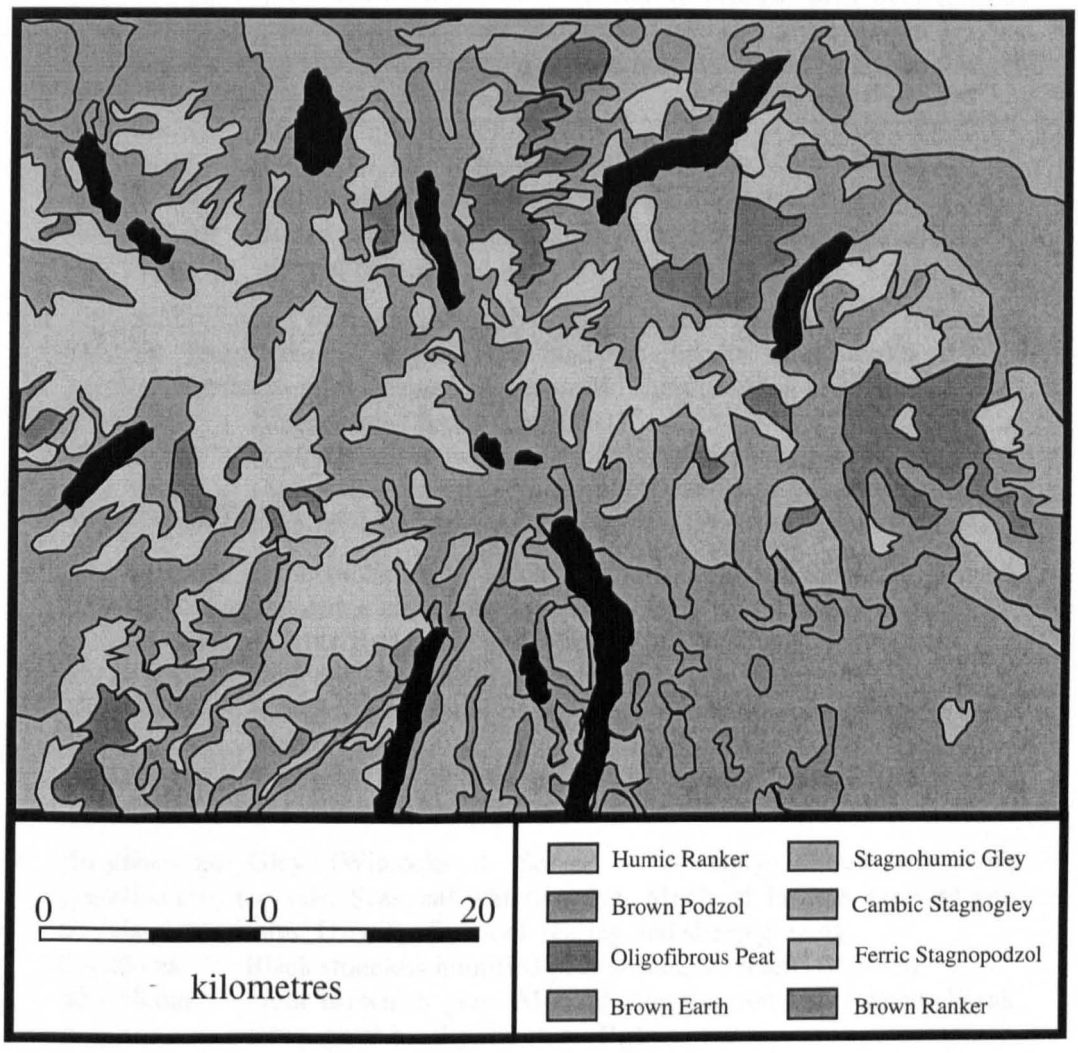
Figure 2.2. - A simplified geological map of the study area



2.2.3. Soils

The chemistry of the surface waters in a catchment is likely to be as much affected by the soils overlying the solid geology as by the underlying rock itself (Section 1.2.2). The central portion of the Lake District consists of nine soil series covering eight major soil types (Figure 2.3), but there are appreciable areas of bare rock in most of the catchments due to the glacial history of the area.

Figure 2.3 - A simplified soils map of the study area



A brief description of the soil types and soil series (in brackets) found in the study catchments follows. Soil details[#] are quoted from the Soil Survey of England and Wales (Avery, 1980), or more specifically the Soil Survey of Northern England (Jarvis *et al.*, 1984a,b).

- Humic Ranker (Skiddaw Series) – Generally above 450m on moderately steep slopes or crags. Cold, wet and exposed land makes improvement difficult. Vegetation is usually *Nardus* grassland, where rough grazing dominates.

  1 – 0 cm Root mat of Sheep's fescue, heather and lichen
  0 – 10 cm Humified peat with moderate/fine granular structure (Oh)
  At 10 cm Metamorphosed Greywacke or Siltstone

[#] **Glossary of Soil horizons:**

Oh – Organic horizon (well decomposed)	Om – 'Raw' organic material	Ap – Ploughed 'A' horizon
Apg – Gleyed ploughed 'A' horizon	Ah – Mineral or Organic 'A' horizon	E – Eluviation horizon
Eg – Gleyed 'E' horizon	B – 'B' horizon	Bh – Organic 'B' horizon
Bt – 'B' horizon with illuvial clay	Bs – 'B' horizon with Fe/Al oxide	Bg – Gleyed 'B' horizon
BC – Transitional zone	BCg – Gleyed transitional zone	C – Weathered rock

- Brown Podzol (Malvern Series) – Soils formed in shallow drift over igneous rocks of varying acidity. Craggy and bouldery slopes are largely rough grazing land. On less steep slopes, improved grassland may dominate. Suited to forestry rather than agriculture.
  0 – 5 cm Black loamy peat (Oh)
  5 – 25 cm Brown, slightly stony sandy silt loam (Ah)
  25 – 60 cm Yellowish red, very stony sandy silt loam (Bs)
  60 – 115 cm Brown extremely stony sandy loam. Blocky and angular (BC)
  At 115 cm Igneous bedrock

- Oligofibrous peat (Winter Hill Series) – Found in peat-covered hills. Almost all soils are deep, wet and organic. The land has little or no agricultural value because of wetness, unpalatable vegetation and short growing season.
  0 – 10 cm Black, semi-fibrous peat (Om1)
  10 – 40 cm Dark reddish brown semi-fibrous / amorphous peat (Om2)
  40 – 70 cm Dark reddish brown semi-fibrous peat. Platy structure (Om3)
  70 – 120 cm Dark reddish grey semi-fibrous peat. Massive structure (Om4)

- Brown Earth (Denbigh Series) – Occur in the foothills of the Lake District. Fine loamy typical brown earth covering much of the land. Forest clearance has left only scattered woodland hence agriculture (improved land) dominates.
  0 – 25 cm Dark brown slightly stony clay loam (Ap / Ah)
  25 – 60 cm Brown slightly stony clay loam. Moderate sub-angular blocky structure (B)
  60 – 100 cm Yellowish brown very stony clay loam. Massive structure or in situ slate or mudstone (BC)

- Stagnohumic Gley (Wilcocks 1 Series) – Strongly gleyed soil with peaty/humose topsoils. Seasonal waterlogging. Much of land is exposed and moorland dominates. Used for livestock rearing and sheep grazing.
  0 – 20 cm Black stoneless humified peat or humose loam (Oh / Ah)
  20 – 50 cm Light brownish grey. Mottled slightly stony clay loam. Weak sub-angular blocky structure (Bg)
  50 – 100 cm Grey with ochreous mottles. Moderate stony clay loam. Weak medium blocky structure (BCg)

- Cambic Stagnogley (Cegin Series) – Seasonally waterlogged loam cambic stagnogley soils. Artificial drainage is required for improvement. Some land is forested but grass growth dominates.
  0 – 20 cm Dark greyish brown slightly stony silty clay loam (Bg)
  20 – 50 cm Light brownish grey. Mottled slightly stony silt clay loam (Bg)
  50 – 100 cm Light grey with ochreous mottles. Moderately stony silt clay loam. Strong coarse prismatic structure (BCg)

- Brown Ranker (Powys Series) – Soils are shallow and well drained. Found mainly on Silurian rocks. Permanent grassland dominates except where steep and rocky slopes preclude machinery where forests dominate.
  0 – 25 cm Dark brown slightly stony clay loam (Ap / Ah)
  At 25 cm In situ slate or mudstone

- Ferric Stagnopodzol (Hafren Series) – Most have peaty surface horizons. Land is mainly steep middle and upper valley sides. Sheep grazing and forestry are the main land use. Much of the land is unenclosed.

0 – 10 cm	Dark reddish brown stoneless semi-fibrous peat (Om / Ah)
10 – 30 cm	Greyish brown mottled. Slightly stony clay loam (Eg)
30 –45 cm	Strong brown. Slightly stony sandy silt loam / clay loam (Bs)
45 – 60 cm	Yellowish brown very strong sandy silt loam (BC)
At 60 cm	In situ silty shale (C)

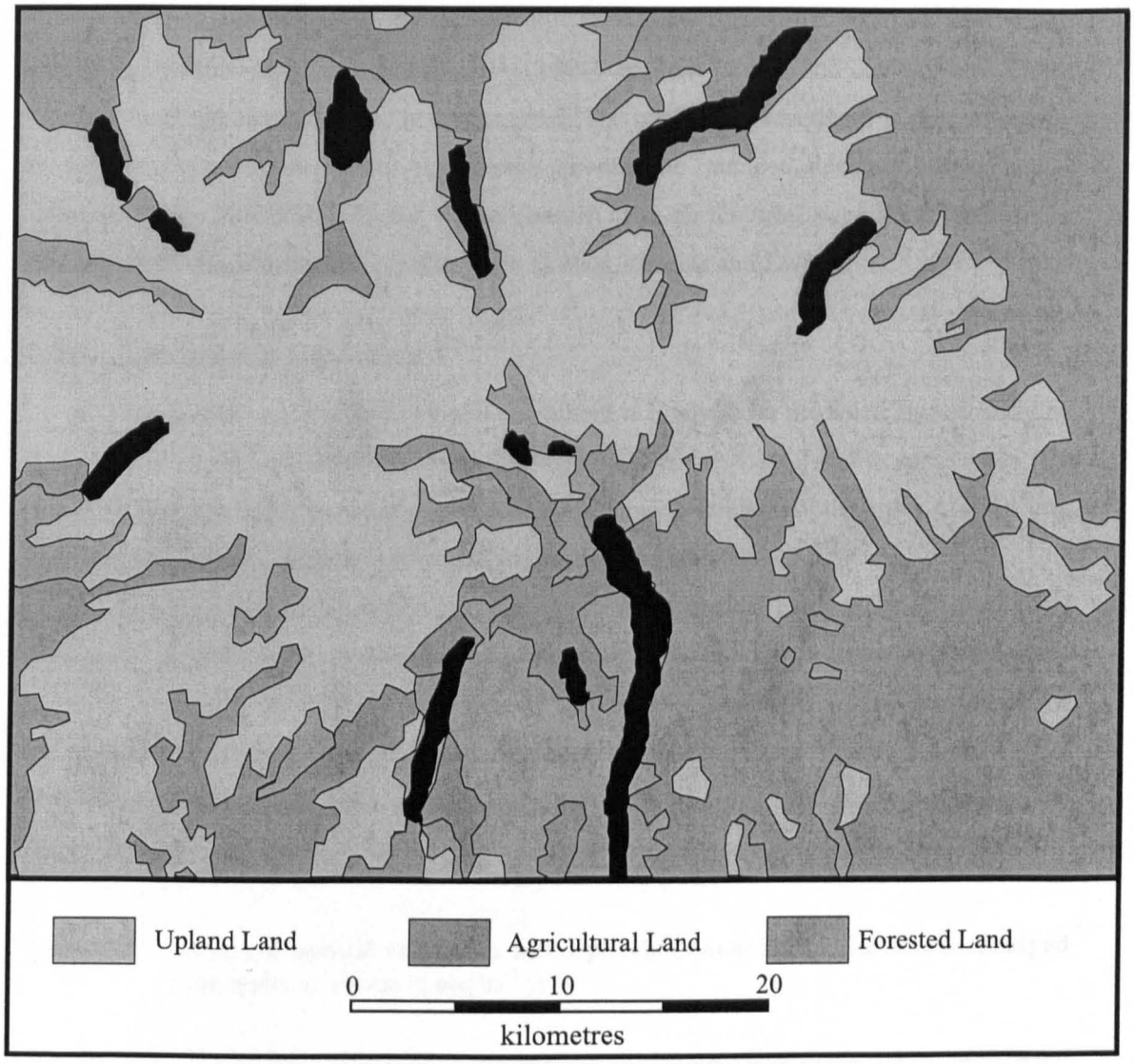
The majority of the study area is made up from four soil types, which essentially separate into two organic (i.e. rankers and peats) and two mineral soils (i.e. podzols and brown earths). Of the organic soils, some are extremely thin (for example, humic and brown rankers) because the underlying rock type and physical conditions prevent a significant amount of weathering occurring, whilst other soils have extremely thick organic layers (for example, Oligofibrous peat) because the physical conditions prevent the occurrence of rapid decomposition. Of the mineral soils, the upper horizons of some have been subjected to significant leaching (for example, Brown podzols), whilst other soils are freely draining and extremely fertile for use by the agricultural or forestry industry (i.e. Brown earths). In general, the organic soils tend to have lower hydraulic conductivity and infiltration rates (i.e. little or no water movement except in the upper few centimetres) than mineral soils. Therefore, the processes within, and the chemistry of, the deep soil horizons may be less important for controlling streamwater chemistry.

2.2.4. Land Use & Vegetation

The water chemistry of streams is essentially imparted by weathering reactions in the soils and the underlying rock (Section 1.2.1 and 1.2.2) and atmospheric deposition (Section 1.2.4). However, as previously discussed in Section 1.2.3, the water chemistry can be significantly modified by land use practices, particularly agricultural liming (for example, papers by Parry *et al.*, 1982; Bricker and Rice, 1989; NRA, 1992a) and scavenging of atmospheric aerosols and particles by trees (for example, papers by Nisbet, 1990; Hornung and Adamson, 1991; Neal *et al.*, 1992b,c). Therefore, the land use and vegetation of the study area are key parameters to consider when discussing the controls on the water chemistry of the study streams.

The central portion of the Lake District consists of three abridged land use types (Figure 2.4). These were identified from the ten land cover types found within the study area using the Land Cover map of Great Britain (see Section 4.2.2. cf. Fuller *et al.*, 1994a,b).

Figure 2.4 - A simplified land use map of the study area



The majority of the land use in the Lake District is upland vegetation, but there are significant areas of agriculture and forestry in the south-east of the study area. At this point it would be useful to note that these areas coincide with the Silurian Slates (Figure 2.2) and will thus become important when discussing the geological / land use controls on water chemistry (Section 4.3.2). Areas of upland vegetation are usually 'pristine' or used for rough grazing, forested areas are either ancient woodland or more commonly conifer plantations, and agricultural areas are used for more intensive sheep and cattle farming. Therefore, the modification to streamwater chemistry should be marked in agricultural and forested areas, and negligible in upland vegetation areas. However, there have been notable changes in the land use and farming practices of the area in the past few decades and this may have resulted in an alteration of the area's streamwater chemistry. The method and degree of land use change is fully discussed in Section 2.2.6.

Upland vegetation is dominated by *Pteridium* (bracken), *Calluna* and *Erica* (heather), *Nardus* and *Festuca* (upland grasses) in drier areas, and *Juncus* and *Carex* (sedges), and *Sphagnum* (moss) in wetter areas. The coniferous woodland is predominantly *Picea* (spruce) and *Pinus* (pine) plantations, whereas the 'ancient' deciduous woodland is *Quercus* (oak), *Betula* (birch) and *Fagus* (beech). The agricultural vegetation tends to be dominated by more 'palatable' grasses such as *Poa*, *Bromus* and *Lolium*.

2.2.5. Atmospheric Deposition

The surface water chemistry of a catchment is likely to be modified significantly by the influx of strong acid anions from the atmosphere (Section 1.2.4), and in some cases (for example, streams with low base cation loads) this may overshadow the roles of land use, soils and the underlying rock in resultant streamwater chemistry.

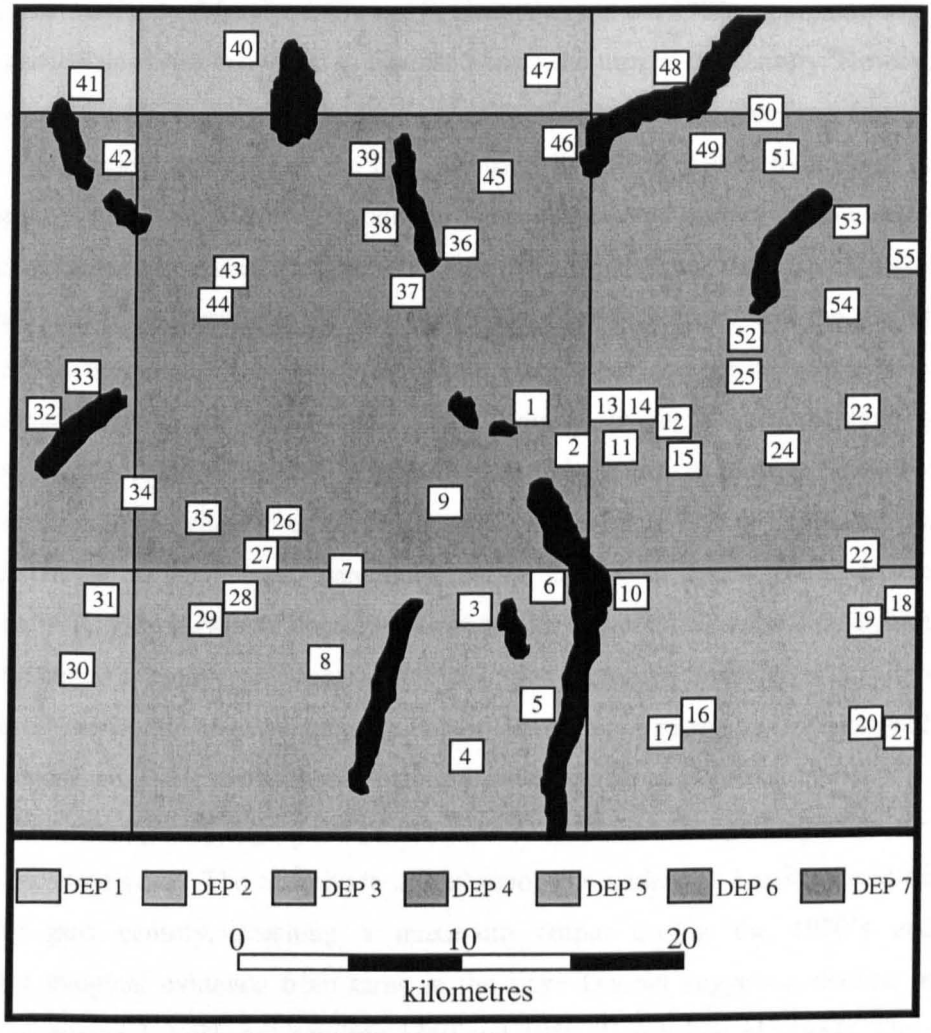
The 20 x 20 km deposition grid squares used for critical loads work (CLAG, 1995; Hall *et al.*, 1995a) were used to estimate the amount of acid deposition the study area receives. Using the 20 x 20 km grid squares as a starting point, the central portion of the Lake District was categorised into seven abridged 'deposition loads' (Table 2.1 and Figure 2.5). A full explanation of the monitoring programme, the methods used to calculate the annual deposition flux and the limitations of data at this scale are given in Section 4.2.1d.

Table 2.1 - Average annual values for atmospheric deposition in the seven abridged categories. (Values in keq ha^{-1} yr^{-1})

Loading	TOTBC	NMBC	NOx	NHx	TOTS	NMS
DEP 1	0.7	0.2	0.4	0.7	1.0	0.8
DEP 2	0.9	0.3	0.4	0.7	1.4	1.1
DEP 3	1.1	0.4	0.5	1.0	1.7	1.4
DEP 4	1.3	0.3	0.5	0.9	1.8	1.3
DEP 5	1.4	0.4	0.6	1.0	2.1	1.6
DEP 6	1.7	0.5	0.8	1.7	2.5	1.9
DEP 7	2.3	0.6	1.0	1.8	3.1	2.3

A series of problems have been identified when attempting to use this national data at a local (or catchment) scale (Section 4.2.1d), but the absence of a higher resolution dataset means the data used is the best available.

Figure 2.5 - A map of the deposition load categories used in the study, and showing location of study sites.



According to Figure 2.5, the majority of the study sites in the Lake District receive high deposition loads (i.e. 10 sites receive DEP5, 16 sites receive DEP6 and 14 sites receive DEP7). In contrast only 15 sites receive the four lowest deposition loads (i.e. DEP1 to DEP4). In the past few decades there have been marked changes in the atmospheric deposition received by the area and this may have resulted in an alteration of the area's streamwater chemistry. Any changes to streamwater chemistry should be more pronounced in 'high' deposition areas than in 'low' deposition areas. The estimated changes in the level of atmospheric deposition received by the Lake District are fully discussed in Section 2.2.6.

2.2.6. Changes in Land Use and Climate

Land use and management practices have significantly changed in the Lake District during the last hundred years. For example, lime was applied to many upland sites to improve the quality of the soil, which increased their agricultural worth. According to work carried out during the Moorland Change Project (Parry *et al.*, 1982), approximately 10% of rough pasture has been converted to farmland since the turn of the century. However, since the 1970's a change in the government's agricultural policy has resulted in a further change to the management practices of the Lake District. Robinson (1984) found that there had been approximately an 80-90% reduction in the application of lime in the Duddon and Esk area since the withdrawal of the lime subsidy in 1976. In addition, cattle stock was changed from hill breeds to prime quality beef stock in the valley bottoms and the use of nitrate fertiliser has increased. As a result, significant amounts of grazing land have been lost in higher areas due to the large labour costs required to remove encroaching bracken. However, the increase in 'natural' vegetation caused by a loss to farming land is offset by the conversion of moorland to conifer plantations. As much as 12% of natural moorland has been converted to coniferous plantations in the last forty years (Nature-Conservancy-Council, 1987). This may have severe implications for the streamwater chemistry of the area in the future, as a number of authors have observed increased levels of acidity in streams after the conversion to large plantation schemes (for example, papers by Ormerod *et al.*, 1989; Cannell and Cape, 1991; Hornung and Adamson, 1991; Neal *et al.*, 1992b,c, 1995).

The atmospheric deposition of the Lake District has changed significantly during the last hundred years. The magnitude of anthropogenic emissions has increased markedly over the past century, reaching a maximum output during the 1970's and 80's. Palaeolimnological evidence from tarns in the Lake District suggest a decline in water quality of around 1.0 pH unit between 1850 and 1980 (Haworth *et al.*, 1987). The authors attributed this pH decrease to the accompanying increase in acid emissions and deposition during this period. Since then, however, national emissions of sulphur dioxide have halved since 1970 and quartered since 1990. In contrast, emissions of nitrogen oxides have remained relatively constant since 1970 (UKRGAR, 1997). Despite the rapid reduction in acidic emissions, improvement in water quality in the Lake District has been very variable over the past 20 years. Some sites have apparently returned to similar water quality to that estimated for pre-industrial times, whilst others have shown negligible improvement during this period (Tipping *et al.*, 1998).

2.2.7. Choice of study sites

Approximately 100 streams in the Lake District were initially selected from maps of the region's topography, drainage network and geology. After a reconnaissance survey in March 1996, only 55 of the original 100 stream catchments were selected for use in the study with the size of these varying between 0.3 and 11.7 km^2. The sites were chosen according to the following criteria:

1. Stream catchments should be dominated by one of the major geological groups in the study area.
2. Access to stream site should not involve more than 30 minutes walk from the nearest road, parking space or 'usable' dirt track. In addition, access or sampling should not present any danger to human life (i.e. sheer drops, crossing slippery rocks, stream too deep or fast etc).
3. Human impact (i.e. fences, effluent pipes, canalised channels, excessive agricultural modification of land etc) should be low to negligible directly upstream of the stream sampling site.

As one of the aims of this project focuses on the importance of geology in influencing water chemistry, most of the stream catchments were underlain by one or two (but occasionally up to three) geological units (Criterion 1). Some of the original sites were discarded due long journey times and dangerous conditions (Criterion 2), whilst others were discarded due to considerations of human disturbance (Criterion 3). The site details can be found in Appendix A.

2.3. Field Methodology

The 55 Lake District streams were sampled over the period May 1996 – March 1997, in six synoptic surveys. The field surveys took place every 2 months and incorporated a variety of flow conditions. Several field measurements were made in the study catchments during the course of this thesis as well as collecting geochemical samples. The protocol for these field measurements (Section 2.3.1) and also the collection of streamwater (Section 2.3.2) and rock samples (Section 2.3.3) is outlined below.

2.3.1 Protocol for field measurements

At each stream sampling site, several measurements and observations were made and recorded in a field notebook. Firstly, the date and time were noted and the weather

conditions were placed into seven subjective categories (Sunny, Bright, Fair, Overcast, Drizzle, Rain and Fog/Misty). Secondly, a portable temperature probe was immersed in the streamwater and left to equilibrate. Thirdly, the width of the channel, from the water's edge on both banks, was recorded using a 20m surveyors measuring tape. Fourthly, the channel depth was measured at 0.5m (in small channels) to 1m (in wide channels) intervals using a foldable plastic metre rule. Fifthly, the channel flow was recorded at 5cm below the surface using a MJP Stream Flow Meter – Model MFP51 (Available from MJP–Geopacks, PO Box 23, St Just, Cornwall, TR19 7JS) at each of the points where depth was previously measured. Finally, the temperature reading was taken immediately prior to leaving the site (circa 15-20 minutes after arrival).

2.3.2 Protocol for collection of water samples

Two water samples were taken at each of the 55 sample sites. Samples for major ion and silica analysis were collected in thoroughly cleaned 150ml wide-mouthed polypropylene bottles (Nalgene), whilst samples for pH and alkalinity determination were collected in thoroughly cleaned 50ml glass bottles ('Medical flats').

Water samples were collected from the central portion of the stream approximately 10 cm below the surface. During sampling, bottles were rinsed three times with the streamwater then filled to the top. The lid was tightened underwater to ensure the amount of trapped air was minimal and that the minimum analytical error occurred due to carbon dioxide degassing (see Section 2.4.1a for further details).

After collection the water samples were immediately placed into a cool box containing ice to keep the water temperature below 4°C. At the end of each field day, the water samples were transported to the Institute of Freshwater Ecology, Windermere, and stored in a refrigerator until the end of each survey week. At the end of each survey week, samples were placed in cool boxes containing ice and transported back to the Open University (circa $3^{1}/_{2}$ hours), where they were immediately placed into a refrigerator to await chemical analysis (see Section 2.4 for next steps in the protocol).

2.3.3 Protocol for collection of rock samples

One rock sample was collected at each of the 55 sample sites. The location for the rock collection was found by searching on foot in the proximity of the stream site. This method usually provided a suitable rock outcrop for sampling (i.e. fairly clean with minimal

lichen) within 1km of the stream sampling site. Around 1 to 2 kg of rock sample was collected using a 2lb lump hammer and a wide bolster (i.e. chisel), and stored in a labelled plastic bag. The rock samples were transported back to the Open University and stored in wooden boxes until chemical analysis was carried out (see Section 2.4 for sample preparation and chemical analysis).

2.4. Laboratory Methodology

In addition to carrying out chemical analysis on the geochemical samples, the field measurements required some recalculation. In the field, the streamflow readings were recorded as revolutions per minute (r.p.m.). The following equation was provided with the flow meter by the manufacturer (MJP Geopacks) and used to recalculate the velocity into metres per second :-

$$V = (0.144 * C) + 5$$

where V is the velocity of the stream section (in $m^1 sec^{-1}$); and
C is the number of counts (i.e. revolutions per minute).

Usually discharge is calculated in the following way – mean depth is multiplied by mean width and then multiplied by the mean velocity. However, velocity within a stream varies considerably due to friction with the bed and sides, as well as the effect of sinuosity, obstructions and constant depth changes (i.e. riffle and pool channels). Most of the streams in this study fall into the riffle and pool category, which vary between shallow areas of high velocity (i.e. riffles) and deep areas of low velocity (i.e. pools). Therefore, it is quite possible that measurement locations may have been only at deep points (i.e. an underestimation of velocity) or shallow points (i.e. an overestimation of velocity). For this reason, the stream was divided into 0.5 to 1m sub-sections to give a more accurate indication of stream flow by measuring the flow in each section rather than just taking a single flow reading. The discharge of the stream was then calculated using the following equation:

$$Q = \Sigma (W_i * D_i * V_i)$$

where Q is the stream discharge (in $m^3 sec^{-1}$);
W_i is the measured width of the *i*th section (in m);
D_i is the measured depth of the *i*th section (in m); and
V_i is the measured velocity of the *i*th section (in $m^1 sec^{-1}$).

After the collection of samples from the field, certain laboratory protocols had to be observed during chemical analysis. The methods used for preparing samples prior to chemical analysis are outlined for streamwater (Section 2.4.1) and rock samples (Section 2.4.2).

2.4.1. Water chemistry laboratory methods

Since the duration of each survey was 7 days, chemical analysis of the samples occurred between 2 and 14 days after collection. The samples were kept refrigerated at 4°C and equilibrated to room temperature prior to all chemical analyses. The water samples were subjected to four separate methods of chemical analysis: pH determination (Section 2.4.1a), Gran alkalinity determination (2.4.1b), major cations and anions determination by ion chromatography (Section 2.4.1c) and silica determination (Section 2.4.1d).

a. pH determination

pH was determined using a Mettler Toledo system with Auto Temperature Calibration (ATC). Full details of the principles behind pH determination can be found in Appendix B.

The pH electrode was calibrated using pH 4.0 and pH 7.0 buffers prior to analysis and the accuracy was checked by measuring the pH of the buffer solutions every 10 samples during analysis. Water samples were poured into a clean 100ml Pyrex® beaker and the pH electrode was immersed in the sample. The pH was recorded immediately after stirring and at the quiescent stage (i.e. after no change in the pH reading for 30 seconds).

b. Gran alkalinity determination

The alkalinity determination was carried out whilst the sample used for pH determination was in the beaker. Alkalinity was determined by Gran titration (Gran, 1952) using the Mettler Toledo pH electrode. Full details of titrant preparation and the principles behind Gran Alkalinity can be found in Appendix B.

A solution of acid was added to the sample in 0.1 ml intervals and mixed with a magnetic stirrer until a pH $\leq$ 4.5 was reached. The exact pH and number of millilitres titrated were recorded in a notebook. The titrant was then added to the sample in 0.1 ml intervals until a pH $\leq$ 4.0 was reached. Again the exact pH and number of millilitres titrated were recorded in a notebook. The process was repeated with the titrant added in 1.0 ml

intervals until a pH ≤ 3.0 was reached. The Gran alkalinity of the water samples was calculated from titration data using a series of equations (see Appendix B for full details).

c. Ion chromatography

Major cation and anion determination took place using a Dionex DX100 ion chromatograph system. Full details of eluent solution and standard solution preparation, the equipment used and the principles behind ion chromatography can be found in Appendix B.

Samples for major ion analysis were filtered using 0.2 μm Whatman syringe filters into 5 ml sample vials prior to analysis. The sample vials were rinsed three times with filtered streamwater to prevent any contamination (e.g. airborne dust) that may have been present in the vials. Separate analyses were performed for anion and cation determination (see Appendix B). Internal anion and cation standards were made up on the day of the sample run and standards from the Institute of Hydrology, UK, were incorporated for inter-laboratory quality control (see Appendix B for methods, and Appendix C for standard data).

d. Silica determination

The dissolved silica content of the streamwater was determined photometrically by molybdate-reactive analysis using the reference method (Webber and Wilson, 1964). Full details of reagent solution and standard solution preparation, the methods and equipment used and the principles behind molybdate-reactive analysis can be found in Appendix B.

During silica analysis, the samples are diluted with deionised water and three analytical reagents are added at separate time intervals. The samples are left to react with the reagents for 20 – 60 minutes, and then measured photometrically. Internal standards were made up on the day of analysis (see Appendix B for methods, and Appendix C for standard data).

2.4.2. Whole-rock chemistry laboratory methods

After the collection of samples from the field, the rock samples required some pre-preparation prior to sample preparation for chemical analysis. The rock samples were broken into manageable pieces using a hydraulic splitter. A small portion of each sample was kept intact for archiving. In the workshop, the weathered surface (weathering rind) was cut off using an abrasive disk saw. Both the weathered and the fresh fractions were reduced to chips of less than 5 mm diameter using a jaw crusher, which was thoroughly cleaned between samples to avoid cross-contamination. A representative sample, obtained by

coning and quartering, was powdered in an agate ball mill for 20 minutes, until the sample was reduced to fine powder. The intact rocks, the chipped fraction and the powdered fraction are archived in the Department of Earth Sciences rock store at The Open University.

The methods used for preparing samples prior to chemical analysis are outlined below for trace elements (Section 2.4.2a) and major elements (Section 2.4.2b). The samples were prepared and analysed using the Open University's in-house reference method (Webb and Watson, 1996). The operating conditions of the XRF equipment are also contained in this publication.

a. Determination of Trace elements using X-Ray Fluorescence analysis

For trace-element analyses, approximately 10 g of rock powder was mixed with binding agent and poured into a 3 cm diameter pellet mould. The pellet was pressed to a pressure of 7 – 9 tons per square inch and dried overnight in an oven at 110°C. The pellet mould was cleaned thoroughly between samples to prevent cross-contamination. Internal standards were made up on the day of the sample run and standards from the US Geological Survey were incorporated for inter-laboratory quality control (see Appendix B for methods, and Appendix C for standard data). Full details of the operating conditions for the equipment used and the principles behind XRF analysis for trace elements can be found in Appendix B.

b. Determination of Major elements using X-Ray Fluorescence analysis

For major-element analyses, approximately 3 g of rock powder was placed in a clean porcelain crucible and dried overnight at 110°C. The dry sample was allowed to cool for 15 minutes in a dessicator (to prevent absorption of atmospheric moisture). Exactly 0.7000g of dried rock powder was mixed with 3.5175 g of fluxing agent in a platinum crucible using a clean plastic rod. The crucible was placed into a furnace at 1100°C for 15-20 minutes and then the molten rock was poured into a heated brass mould to form a 3 cm diameter glass disc.

The loss on ignition of the sample was determined to quantify the volatile content (i.e. H_2O and CO_2) of the sample. An alumina crucible was pre-heated in a furnace at 1000°C for 20 minutes. After cooling for 10 minutes, 1-2 g of dried rock powder was weighed accurately into the alumina crucible and placed back in the furnace at 1000°C for 30-45 minutes. The crucible was reweighed after cooling for a further 10 minutes and the weight loss was recorded.

Again, internal standards were made up on the day of the sample run and standards from the US Geological Survey were incorporated for inter-laboratory quality control (see Appendix B for methods, and Appendix C for standard data). Full details of the operating conditions for the equipment used and the principles behind XRF analysis for major elements can be found in Appendix B.

2.5. Data Analysis

The geochemical data was analysed using statistical methods and by the process-based model MAGIC. The data were subjected to two separate methods of statistical analysis, multiple regression analysis and principal component analysis. In addition, the MAGIC model was applied to the majority of the study catchments to estimate weathering rates and soil chemistry. Full details of the methods and results obtained from the statistical analyses and MAGIC runs can be found in Chapter 5 (Sections 5.2 and 5.3). Here, only a brief discussion takes place concerning the principles, underlying structure and assumptions of multiple regression (Section 2.5.1a), principal components analysis (Section 2.5.1b) and the MAGIC model (Section 2.5.2).

2.5.1. Statistical Analysis

One of the aims of the statistical analyses was to ascertain whether the variation in water chemistry at the study sites could be described by catchment characteristics and, if so whether catchment data could be used to predict the water chemistry. The most appropriate approach to begin this process was multiple regression.

a. Multiple Regression Analysis

Multiple regression analysis is a useful and powerful statistical tool. It has been widely used for a multitude of applications. For example, many acidification studies (including Webb, 1984; Lynch and Dise, 1985; Kernan, 1995; Kernan *et al.*, 1998) have used multiple regression, as well as many other medical, ecological and geological studies available in the scientific literature. This section describes the principles, underlying structure and assumptions of multiple regression analysis.

PRINCIPLES

In this case, the water chemistry data are the response, dependent or Y variables, and the catchment characteristics are the predictive, independent or X variables. In a simple linear

regression, the relationship between a single Y and a single X variable is examined, where Y is some function of $X \pm$ statistical error. It assumes that experimental error is in the Y measurements, with X values being exact. By plotting X and Y against each other, simple linear regression produces a line through the scattered datapoints using the following equation:

$$Y = \alpha + \beta X + \varepsilon$$

where	Y	is the response or dependent variable;
	α	is the intercept of the line with the y axis;
	β	is the slope of the line;
	X	is the predictive or explanatory variable; and
	ε	is the error term.

The best technique for estimating α and β uses the method of least squares. The least squares method calculates a value for the model where the sum of all squared errors is as small as possible.

However, the variation in the distribution of a Y variable is often a function of more than one X variable. In multiple linear regression the response (or Y) variable is predicted by the values of two or more predictive (or X) variables. This is described using the following equation:

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 \ \ldots\ldots\ldots\ldots + \beta_n X_n + \varepsilon$$

where	Y	is the response or dependent variable;
	α	is the intercept of the line with the y axis;
	β_1 - β_n	are the slopes of the line;
	$X_1 - X_n$	are the predictive or explanatory variables; and
	ε	is the error term.

This technique finds the coefficient of all the X variables with the minimal sum of squares error. The regression model implies that X_1 to X_n predict Y to some extent. The overall accuracy of the prediction is reflected by the R^2, which is the proportion of the variation explained by the X variables in the equation.

A further development of multiple regression is the stepwise regression method. In the stepwise method, a computer builds the regression in stages by adding and taking out X variables one at a time until all the possible X variable combinations have been tested. A value is given to the computer to denote the level of statistical significance required (i.e. $p \leq 0.05$), and the stepwise method produces a model which explains the highest proportion of the variation in Y using only the statistically significant X variables.

ASSUMPTIONS AND POTENTIAL PROBLEMS

There are several basic assumptions that need to be adhered to when using multiple regression analysis. Explanatory (or *X*) variables should not be significantly inter-correlated (i.e. exhibit multicollinearity), data should be normally distributed and there should be no pattern between the residuals and *Y* estimates or *X* values. Residual plots are used to assess whether these assumptions (i.e. randomness, constant variance and normality) are fulfilled (see Appendix H). Most problems arise due to the use of 'ill-conditioned' data (i.e. data that violates at least one of the assumptions). Although this does not directly affect the fitting of the model, it limits the statistician's ability to make inferences from the data.

One potential problem is that the catchment characteristics in this study are analysed as a percentage (i.e. areal coverage of the catchment) so the sum of the percentages always equals 100. This introduces the problem of data multicollinearity because the last independent variable is perfectly predicted by the previous variables. It has been suggested that to remedy this problem one of the variables should be excluded from the regression analysis, which effectively incorporates it into the intercept term (Watson, 1969). However, in this case, variables with high multicollinearity are automatically eliminated from the regression equation by the computer.

Another potential problem is the use of automatic procedures to select the *X* variables (i.e. the stepwise method). These procedures do not take into account specialist knowledge about the data and the model selected may not be the best from a practical point-of-view. For example, the 'best-fitting' model might only have a slightly higher R^2 value than one with alternate variables that are (i) easier to measure; (ii) may be ascribed more clearly to controlling processes; and (iii) are fewer in number. For this reason, the initial multiple regression equations are best considered a guide rather than the final model (Section 5.2.2).

b. Principal Components Analysis

Multiple regression provides information about the relationships between *X* and *Y* variables and looks to predict the value of *Y* using a number of *X* variables. However, in principal component analysis, a combination of *X* variables that account for the largest proportion of the total variability using a single measurement are looked for. Although the technique still assumes normality, there are few assumptions that need to be adhered to during analysis, which is one of the strengths of principal component analysis over multiple regression.

The linear combination of variables that corresponds to the largest amount of variability is called the first principal component (or axis 1). The second principal component (or axis 2) accounts for the most variability after the effect of the first has been removed, the third principal component accounts for the most variability after the first and second have been removed and so on. Each axis is described by an eigenvalue (λ), which indicates how much of the variation in the data can be explained by that particular axis. Theoretically, there are as many principal components as there are variables. However, in practice, the first four axes usually explain the majority of the original total variance and the statistical explanation of the remaining axes can usually be ignored.

The determination of principal components uses the eigenvalues of a correlation matrix. These are mathematical objects associated with the matrix with origins in the algebra of linear transformations. In practice, the eigenvalues need to be calculated by a computer because the mathematical processes involved are very complex (Cohen, 1988). The vector of the correlation coefficients gives the degree of correlation each variable has with a specific component, and uses the following formula:

$$V_c = \frac{\sqrt{\lambda}\,\mathbf{e}}{|\mathbf{e}|}$$

where	V_c	is the vector of correlation coefficients;
	λ	is the eigenvalue;
	e	is the eigenvector;
	$\|\mathbf{e}\|$	is the square root of the sum of the squares of **e**'s co-ordinates (i.e. denotes the length of **e**).

The identification of principal components may in itself provide adequate information as 'stand-alone' data analysis. Alternatively the resulting principal component axes may be entered into a multiple regression to act as a surrogate for several variables (see Section 5.2.4).

The actual statistical analyses take place in Chapter 5, where multiple regression analysis, principal component analysis and a combination of both techniques are used to assess whether the variation in water chemistry of Lake District streams is a function of the catchment characteristics. In addition, an empirical model is developed using 'key' catchment parameters to predict water chemistry.

2.5.2 MAGIC model structure

One of the controls on water chemistry is the weathering rate (Section 1.2.1). Accurate weathering rate data is almost impossible to obtain in the field. Usually a

manipulation of weathering occurs in the laboratory by estimating weathering rates under vastly accelerated conditions. This method is widely used in weathering studies but obtaining accurate data with this technique is also very difficult. In this study, the process-based model, MAGIC, was used to estimate weathering rates for the individual study catchments (Section 5.3). This section describes the principles, underlying structure and assumptions of the MAGIC model.

PRINCIPLES AND MODEL STRUCTURE

The MAGIC (Model of Acidification of Groundwater In Catchments) model was created by researchers at the University of Virginia (Cosby *et al.*, 1985a,b,c) in response to the plethora of literature detailing the deterioration of surface waters due to acid deposition. It was specifically designed to perform long-term simulations of the changes in soil and stream water chemistry that occurs in response to increasing acid deposition. It was hoped that the model would provide a more complete understanding of the processes controlling surface water acidification under different scenarios of acid deposition (Jenkins *et al.*, 1997).

MAGIC has its roots in the Reuss-Johnson conceptual system of ionic equilibria in soils (proposed by Reuss, 1980, 1983; and expanded in Reuss and Johnson, 1985), and is a physically based conceptual model that uses a lumped representation of complex catchment scale processes. Mathematical representations of the following 5 'key' soil processes thought to mitigate the effects of acid deposition on surface water quality form the physical basis of the model (Cosby *et al.*, 1984, 1985c, 1986):

- Anion retention by catchment soils (e.g. sulphate adsorption)
- Cation exchange buffering by catchment soils
- Generation of alkalinity by carbonic acid dissociation
- Aluminium mineral dissolution in catchment soils
- Replacement of base cations via mineral weathering

The MAGIC model simulates these natural processes by (a) Using a set of equations to quantitatively describe the equilibrium soil processes and the chemical changes that occur as soil water enters the stream channel; (b) Using a set of mass-balance equations to quantitatively describe the input-output relationships of base cations and acid anions in precipitation and streamwater; and (c) Using a set of definitions that relate to the variables from both sets of equations (Cosby *et al.*, 1984, 1985b). Only a brief overview of the structure and equations are given here. Full details of the 24 equilibrium equations, 8 mass-balance equations and 12 definitions used to make up the underlying structure of the model can be found in Cosby *et al* (1984, 1985b).

The model assumes equilibrium processes in the soil and soil-water are responsible for the observed streamwater chemistry in the catchment. The formation of bicarbonate from dissolved CO_2 and water generates soil-water alkalinity and is described by the following equation:

$$CO_2 + H_2O = H^+ + HCO_3^-$$

The free hydrogen ion produced by the above equation reacts with the aluminium mineral (e.g. gibbsite) in the soil to give:

$$3H^+ + Al(OH)_3 = Al^{3+} + 3H_2O$$

The cation exchange sites in the soil matrix have a higher affinity for trivalent aluminium than di- or monovalent base cations. Therefore, there is an exchange between dissolved and adsorbed phases that is represented as follows:

$$2Al^{3+} + Ca_3X = Al_2X + 3Ca^{2+}$$ (X represents the adsorbed phase of cation)

The net result of these reactions is the production of alkalinity in the form of bicarbonates of the base cations – i.e. $Ca(HCO_3)_2$. As the CO_2 partial pressure (or the availability of base cations on the soil exchange sites) increases, the equilibrium reactions proceed farther to the right resulting in higher alkalinity. When the solution is removed from the soil matrix and exposed to the atmosphere, the CO_2 is degassed and partial pressure falls resulting in an increase in pH but no net change to alkalinity. As the stream loses CO_2 and pH starts to rise, the solubility of aluminium species in the stream is exceeded and aluminium is precipitated in the solid phase. This process retards the increase of streamwater pH as CO_2 degasses, which will lower streamwater pH if exchangeable cations are less available.

The depressed aluminium adsorption by the solid results in a decline in soil and surface water alkalinity, by considering alkalinity thus:

$$ALK = (HCO_3^-) - (H^+) - 3(Al^{3+})$$

When the catchment soil's ability to exchange aluminium decreases, the aluminium and hydrogen ion concentrations increase, causing the net alkalinity of the solution to decline even though the source of bicarbonate is unaffected.

The acidification process is also controlled by the exchangeable base cation supply

in the soil (i.e. their rate of depletion, their rate of resupply from mineral weathering and their rate of leaching loss). Strong acid anions (from precipitation usually) mainly control the leaching rate by moving through the soil and removing base cations. To maintain charge balance, there must be a concomitant increase in cations to balance the increase in anions from precipitation. Normally in acid deposition, anions are deposited from the atmosphere with hydrogen, which will initially replace the base cations at soil exchange sites. As the base saturation of the soil declines, aluminium and hydrogen become more important for maintaining the charge balance and streamwater becomes more and more acidic as deposition persists.

The model undertakes a simple calculation for the concentration of the four strong acid anions in streamwater and soil-water. However, sulphate has an adsorbed phase in the model. The relationship of dissolved and adsorbed sulphate is assumed to follow the Langmuir isotherm, and is represented thus:

$$E_s = E_{max} \frac{(SO_4^{2-})}{C + (SO_4^{2-})}$$

where E_s is the adsorbed sulphate;
E_{max} is the maximum adsorption capacity; and
C is the half saturation constant.

It should be noted that most upland soils in the UK are relatively young (and many are sulphate saturated) and consequently do not strongly adsorb sulphate. Therefore, the values set for the Langmuir isotherm in this study (Chapter 5) are E_{max} = 0.01 meq kg^{-1} and C = 1000 meq m^{-3}. This effectively results in sulphate acting in steady state.

As far as the model is concerned only aluminium and the four base cations (i.e. Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) are involved in cation exchange reactions. These exchange reactions are modelled using a Gaines-Thomas expression (Gaines and Thomas, 1953) for monovalent and divalent cations, and are expressed thus:

For monovalent cations:

$$S_{Al\,Ca} = \frac{\{Ca^{2+}\}^3 E_{Al}^2}{\{Al^{3+}\}^2 E_{Ca}^3}$$

For divalent cations:

$$S_{Al\,Na} = \frac{\{Na^+\}^3 E_{Al}}{\{Al^{3+}\} E_{Na}^3}$$

where $S_{Al\,Ca}$ is the selectivity coefficient (After Reuss and Johnson, 1985);
$\{\}$ represents the ion activities in soil water; and
E is the exchangeable fraction of the ion (Calculated by dividing the base saturation of an ion by the soils cation exchange capacity).

The model gives the base saturation of the soil as the sum total of exchangeable fractions of aluminium and the four base cations in the soil.

$$BS = E_{Ca} + E_{Mg} + E_{Na} + E_K = 1 - E_{Al}$$

In addition, if aluminium exchange equations are combined with aluminium solubility equations, a Gaines-Thomas expression for hydrogen exchange results.

The model calculates the streamwater concentrations from equations for any time the model is run based on the total amount of each ion in the catchment at that time using a mass balance approach. The inputs of acid anions are primarily through atmospheric deposition, whilst the inputs of base cations come from primary mineral weathering. Outputs are by streamwater losses. For each of the base cations and strong acid anions in the model, the mass balance equation can be written in the form:

Using calcium as an example:

$$\frac{dCa_t}{d_t} = F_{Ca} + W_{Ca} - Q * (X) * n$$

where Ca_t is the total amount of calcium in the catchment (eq m^{-2});
F_{Ca} is the atmospheric flux of calcium into the watershed (eq m^{-2} $time^{-1}$);
W_{Ca} is the net uptake-release flux of calcium (eq m^{-2} $time^{-1}$);
Q is the volume flow of the stream;
(X) is the total molar concentration of calcium in streamwater; and
n is the charge of the ion (i.e. for calcium n = 2).

Once the initial conditions have been established, the equilibrium equations are solved for soil-water and streamwater concentrations. The output fluxes are calculated from these concentrations for the first time step. The mass balance equations are integrated over the

time step, which provides new fluxes each time the input of base cations or acid anions into the system changes.

INPUT REQUIREMENTS

The model requires accurate data for certain input parameters, whilst other input parameters can be estimated with negligible side effects to the models accuracy (Jenkins *et al.*, 1997). Required data includes:

- Accurate atmospheric deposition and net uptake-release fluxes for base cations and strong acid anions. These are assumed to be homogeneous over the entire catchment.
- Fluxes are calculated by multiplying the volume of rainfall received by the catchment by the concentrations of ions in precipitation. A correction is required for the atmospheric deposition of sulphate to account for dry deposition.
- Volume of streamflow to calculate output flux.
- Values for soil and streamwater temperature and soil PCO_2.

The model in its simplest form works as follows. Atmospheric deposition enters the soil and equilibrium equations are solved to calculate soil-water chemistry. The water then flows to the stream where the appropriate equilibrium equations are solved to calculate streamwater chemistry. The actual calibration and application of the model to the study catchments can be found in Chapter 5, whilst the full details of the parameter and optimisation files for each study catchment can be found in Appendix G.

CHAPTER 3

Whole-rock chemistry of Lake District catchments

"GEOLOGY, n. The science of the earth's crust -- to which, doubtless, will be added that of its interior whenever a man shall come up garrulous out of a well. The geological formations of the globe already noted are catalogued thus: The Primary, or lower one, consists of rocks, bones or mired mules, gas-pipes, miners' tools, antique statues minus the nose, Spanish doubloons and ancestors. The Secondary is largely made up of red worms and moles. The Tertiary comprises railway tracks, patent pavements, grass, snakes, mouldy boots, beer bottles, tomato cans, intoxicated citizens, garbage, anarchists, snap-dogs and fools."
- 'The Devils Dictionary' by Ambrose Bierce

3.1. Introduction

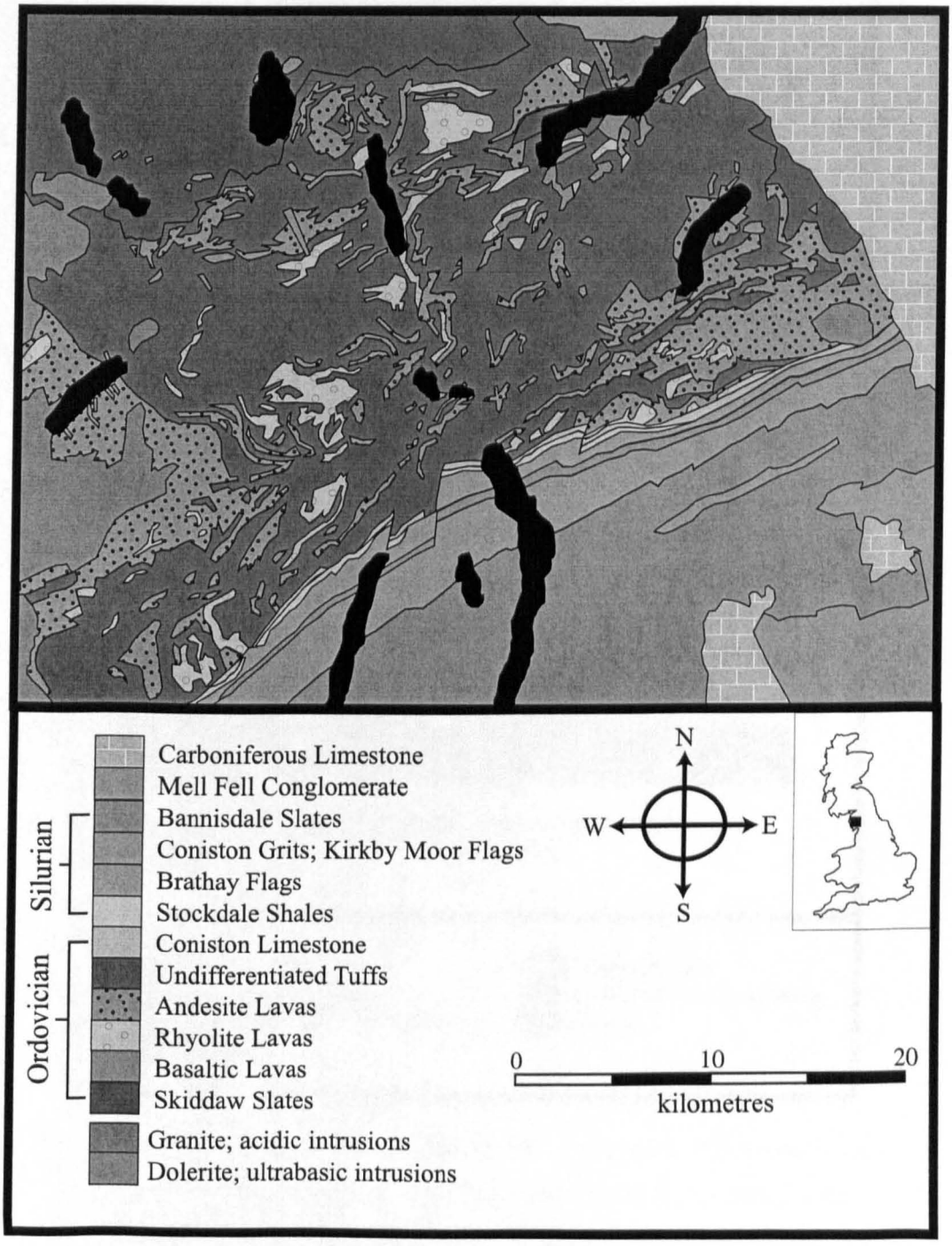
This chapter begins with a brief review of the general geology and the evolution of the Lake District based on published stratigraphic, geochemical and geochronological data (Section 3.2). During the course of this thesis, bedrock samples were collected from the catchments used in the stream chemistry aspect of the project, although the bedrock sample collection sites varied slightly from the stream water collection site (grid references for both sets of sites are in Appendix A). The weathered and fresh fractions of the rock samples were subsequently analysed using X-ray Fluorescence analysis (Appendix B). The rock chemistry data are dealt with in three phases: (1) Major-element geochemistry of the Lake District (Section 3.3); (2) Trace-element geochemistry of the Lake District (Section 3.4); and (3) Determination of weathering patterns from fresh and weathered geochemical data (Section 3.5). In addition, the geochemical data from this study are also compared with other published data from the Lake District, thus allowing the survey results to be put into context (Section 3.3.3).

3.2. Geological background of the Lake District

The Lake District (54°18'N to 54°37'N, 2°38'W to 3°19'W) is situated in the north-west of England. The area is dominated by rocks of Lower Palaeozoic age ranging from the Ordovician to Silurian. The geology may be divided into three major lithological types trending south-west to north-east, which are intruded by large igneous bodies. The

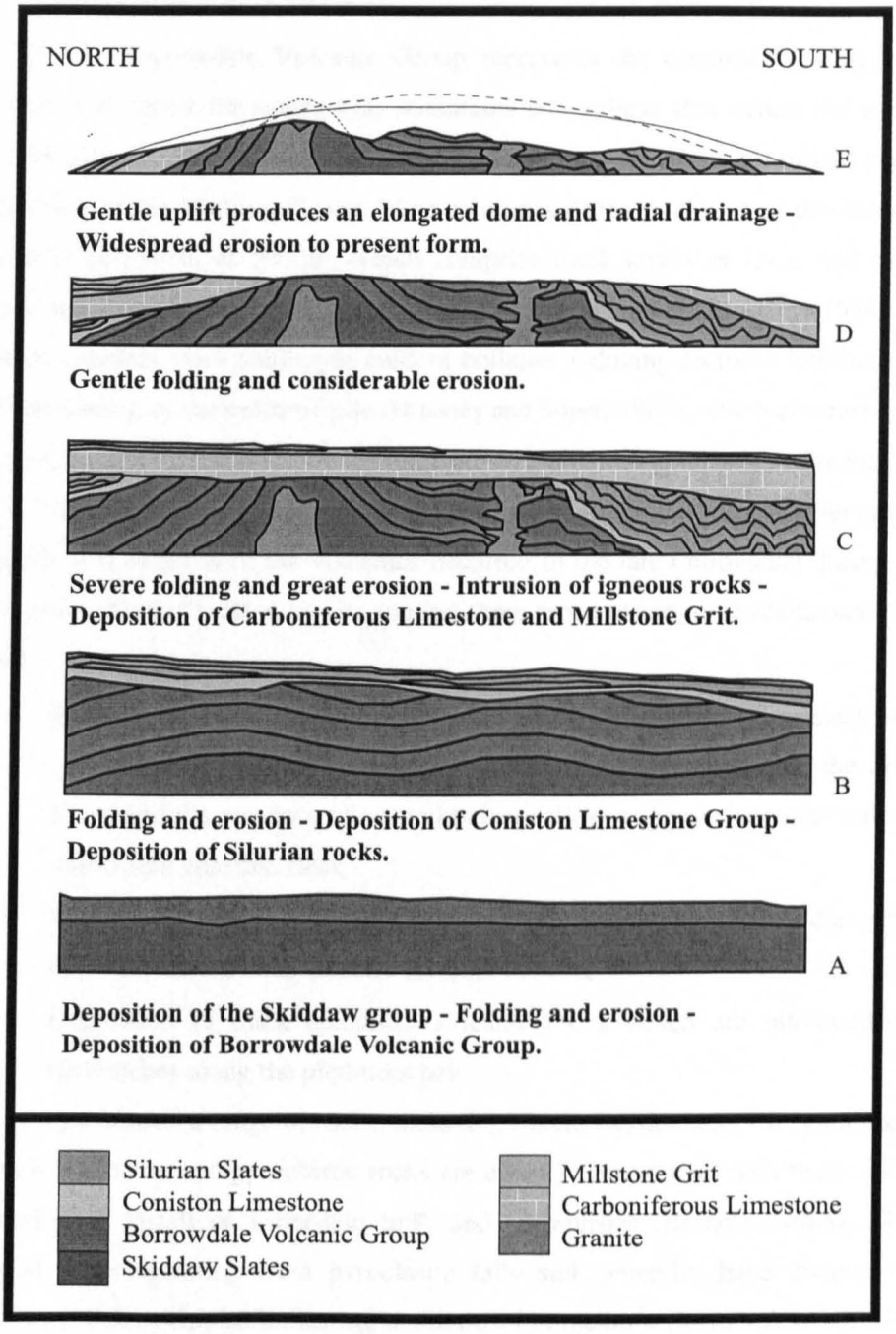
basement geology of the Lake District is illustrated by Figure 3.1. Superficial cover record major disruptions made by the Pleistocene glaciations that resulted in deposition of till and alluvium. Therefore, the till may have a different provenance and chemistry compared to the underlying bedrock. However, the spatial cover of these surficial deposits is relatively small in the study area.

Figure 3.1 - A generalised map of Lake District solid geology



The geological evolution of the Lake District over the past 500 million years may be described by a series of North-South sections (Figure 3.2).

Figure 3.2. - Diagrammatic sections to illustrate how the Lake District was formed (after Taylor et al., 1971).



N-S section A – During the Early Ordovician a sequence of muds, silts and minor sandstones (now the Skiddaw Group) were deposited in a subsiding basin. Early small-scale folds in the sediment originally thought to be tectonic have been identified as slumps in a turbidity current environment (Webb and Cooper, 1988). In addition, large olistotrome rafts

developed during this period, which became detached from time to time and slid downslope, resulting in a chaotic melange of fragments of different ages. Although, the structural and stratigraphical interpretation of the Skiddaw Group is open to much conjecture (Moseley, 1978). It is widely accepted that the group consists of several thousand metres of turbidites deposited on the continental slopes of the Iapetus Ocean with a series of slump and olistotrome raft structures.

The Borrowdale Volcanic Group represents the dominant geology of the Lake District, and forms the spectacular mountains and valleys that makes the area so popular with tourists. It records a period of widespread calc-alkaline volcanism, post-dating the deposition of the Skiddaw Group. Most estimates of the thickness of the volcanic rock are generally in excess of 5000m, which comprise thick layers of lavas and tuffs, some of which were subaqueous, and some of which were subaerial (Moseley, 1978). In addition, volcanic centres were subject to caldera collapse inducing tectonic faulting, block tilting and foundering of the volcanic pile (Branney and Soper, 1988), which contrasts greatly to the areas of bedded tuffs formed by the uniform spread of volcaniclastic sediment.

The age of the group has always been contentious but micro-palaeontological work suggests that eruption of the volcanics occurred in the late Ordovician during the Caradoc (Molyneux, 1988). Detailed studies suggest three broad phases of volcanic activity (Moseley, 1990).

- Effusion of basalt / andesite flows and sills with interbedded primary and reworked pyroclastic deposits. The structures within the clastic deposits, the distribution of flows and the presence of several palaeovalleys suggest the construction of a broad shield-like volcanic field.
- Widespread eruptions of acidic and strongly-welded pyroclastic deposits. These are often associated with volcano-tectonic faulting
- Deposition of thick epiclastic volcanic rocks which are interbedded with acid ignimbrites along the piedmont belt.

The group contains a range of rocks, including basalt, basaltic andesite, andesite, dacite and rhyolite. The lavas and pyroclastic rocks are equally represented, with the pyroclastic rocks consisting of airfall or water-lain tuffs and ignimbrites (Branney, 1988). The tuffs are lithified ash originating from pyroclastic falls and generally have distinct sedimentary structures such as ripples indicating the deposition medium (Moseley, 1990). However, the term tuff describes a wide range of bedded deposits too numerous to label on large-scale maps. Therefore, the heterogeneity of the rocks in this rock group may cause catchment-to-catchment variation in the base cation supply to surface waters.

N-S section B – The layers of lavas and tuffs from the Borrowdale Volcanic Group subsequently suffered considerable erosion and deformation, before subsidence resulted in a marine transgression and the deposition of the Coniston Limestone group in the Late Ordovician (McNamara, 1979). The sequence is complex (Moseley, 1990) and mainly consists of breccia, sandstone, siltstone, chert, nodular limestone and calcareous mudstone, and is approximately 100 metres thick (McNamara, 1979). The brief recurrence of volcanic activity that followed resulted in a 200 metre thick layer that is interpreted as a rheomorphic ignimbrite (Millward and Lawrence, 1985).

Silurian sediments comprising muds, silts and sands were deposited in an elongate subsiding basin collectively known as the "Windermere" group (Moseley, 1990). The "Windermere" group, which dominates the southern Lake District, comprises five different formations, Stockdale Shales, Brathay Flags, Coniston Grits, Bannisdale Slates and Kirkby Moor Flags.

The Stockdale Shales, consists of black carbonaceous shales probably formed in anaerobic conditions associated with a deepening sea, followed by a transition into greenish mudstone representing the slow reversal to aerobic conditions (Ingham *et al.*, 1978). The Brathay Flags, which are 300 metres thick and uniformly grey with alternating pale siltstone and darker graptolite mudstone layers, succeed this formation. Its mode of deposition is a matter of debate (Taylor *et al.*, 1971); competing hypotheses include (i) Formation by tranquil sedimentation in anaerobic conditions; or (ii) The products of turbidity currents (Ingham *et al.*, 1978). The Coniston Grits, which succeed the Brathay Flags, are mostly fine sand-grade turbidites with a greywacke texture and composition. The formation is upto 1700metres thick, and consists of sandstone beds (1-2m) separated by thin layers of mudstone thought to result from a southerly extension of turbidity currents from southern Scotland (Taylor *et al.*, 1971), as indicated by north-west directed flow structures (Norman, 1963). The Bannisdale Slates follow and comprise of a banded facies of dark grey mudstone and stripes of pale siltstone (Moseley, 1990). The formation is an average of 1500 metres thick, and is believed to be, like the greywackes, the product of turbidity currents (Taylor *et al.*, 1971). The Kirkby Moor Flags are often slumped and consist of well-sorted sandstones and siltstones. The formation is upto 900 metres thick, has an entirely shelly fauna and has abundant structures consistent with dewatering (Ingham *et al.*, 1978).

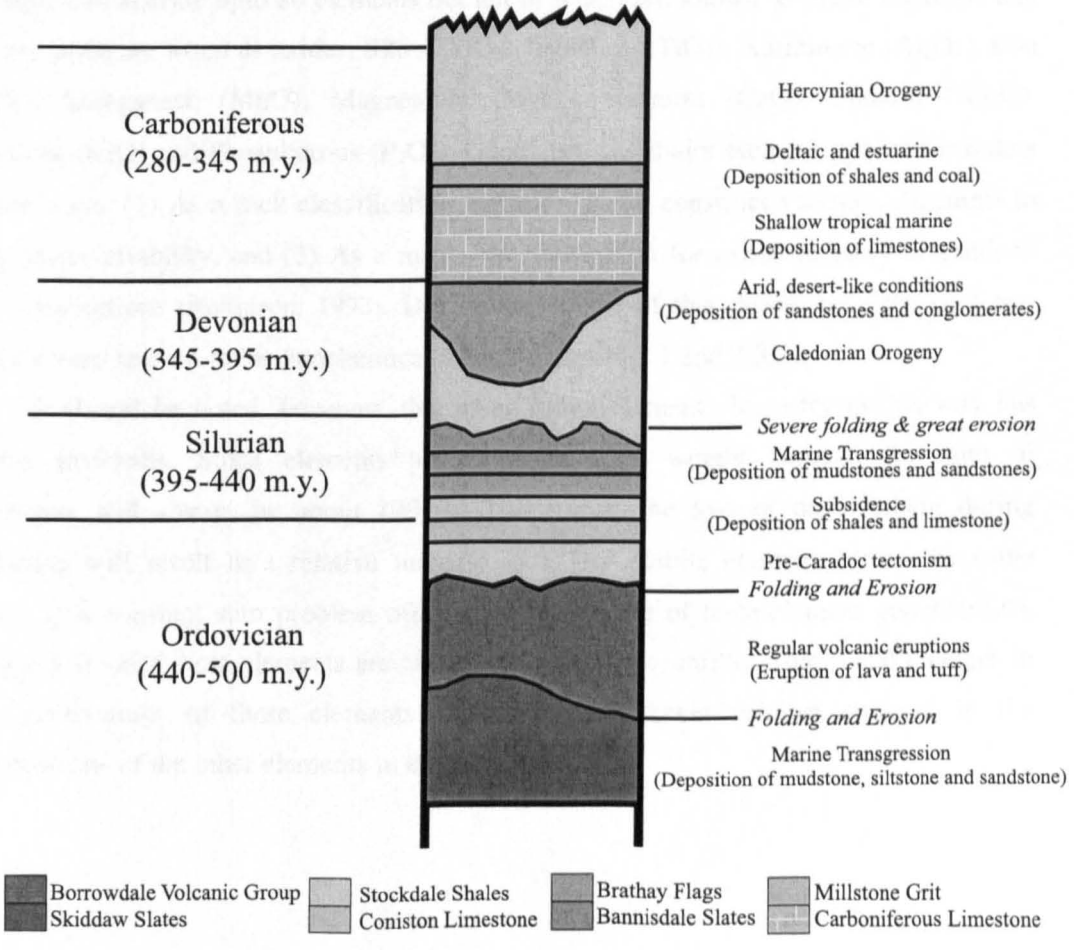
N-S section C – By the end of the Silurian period, active tectonics narrowed the sedimentary basin and culminated in a period of regional folding, known as the Caledonian phase (Taylor *et al.*, 1971). Widespread intrusion of felsic magma accompanied deformation and uplift forming the Eskdale /Shap granites and the Ennerdale granophyre (Firman, 1978).

The period of compression and folding was followed by a marked climatic change to a desert-like environment resulting in the deposition of the Mell Fell Conglomerate (Wadge, 1978). This was followed by Carboniferous Limestone, deposited in the relatively shallow tropical clear-water seas. The deposition has a cyclical nature, which is easily detectable throughout the sequence. The earliest beds contain abundant foraminifera, corals and brachiopods and show clear evidence of near-shore deposition (Mitchell *et al.*, 1978). It has been suggested that the cycles are evidence of eustatic changes of sea level (Ramsbottom, 1973). This was followed by a period when the sea receded and a deltaic environment prevailed, which led to the deposition of the Millstone Grit in the area around Lancaster and Morecambe.

N-S Sections D & E – Quaternary glaciation shaped the mountains to their current form.

A generalised geological succession of the area summarises the geological history of the Lake District (Figure 3.3).

Figure 3.3 - The geological succession of the Lake District and the conditions and events leading to its formation (Moseley, 1978).



The field area of this study is 35 km long in a North-South direction and 45 km long in an East-West direction. This encompasses a wide range in geology from the old slate belt in the North, through volcanic peaks in the central region, into younger slates, sandstones and the surrounding rim of limestone (Lake District dome) in the south. For the purpose of this thesis, the lithology has been grouped into three broad categories, (i) Borrowdale Volcanics; (ii) Skiddaw Slates; and (iii) Silurian Slates (or Windermere group). The validity of this categorisation, based on the geological units of the British Geological Survey, was examined by analysing the individual chemistries of the rock samples (Sections 3.3 and 3.4). This also allowed the inter-group and intra-group diversity to be assessed.

3.3. Major-element geochemistry of the Lake District

The rock samples were subjected to X-Ray Fluorescence (XRF) analysis (see Appendix A for site details). The analytical techniques and geochemical data tables are given in Appendix B and Appendix E, respectively. XRF analysis can detect concentrations over a wide range of sensitivities from 100 % to a few parts per million. This geochemical technique can analyse upto 80 elements but ten of which are known as major elements and by convention are listed as oxides; Silica (SiO_2), Titanium (TiO_2), Aluminium (Al_2O_3), Iron (Fe_2O_3), Manganese (MnO), Magnesium (MgO), Calcium (CaO), Sodium (Na_2O), Potassium (K_2O) and Phosphorous (P_2O_5). Geologists use major element geochemical data in three ways: (1) As a rock classification method; (2) To construct variation diagrams to assess inter-variability; and (3) As a means of comparison for experimentally determined rock compositions (Rollinson, 1993). During the course of this thesis, only the first two methods were applied to the geochemical data (Sections 3.3.1 and 3.3.2).

It should be noted, however, that using major-element chemistry in this way has inherent problems. Since elements are determined as weight percent, the sum of percentages will always be about 100 %. This means the loss of one element during weathering will result in a relative increase in a less mobile element within the same system. This constant sum problem often leads to the use of trace-element geochemistry (Section 3.4) since these elements are calculated as parts per million (ppm) and changes in the concentrations of these elements result in much lower relative changes in the concentrations of the other elements in the rock.

3.3.1. Rock Classification

A large volume of data was produced by the XRF analysis (Appendix E), which was initially used to classify the rocks on the basis of their chemical composition. The most straightforward way of examining major elements is the use of a simple bivariate oxide-oxide plot. Other methods include bivariate ratio-oxide plots, bivariate ratio-ratio plots and triangular (or ternary) diagrams. The usage and interpretation of ternary diagrams must involve a degree of caution as the process of percentage calculation may change the rank order of the means, variances and correlation coefficients within the dataset (Rollinson, 1993).

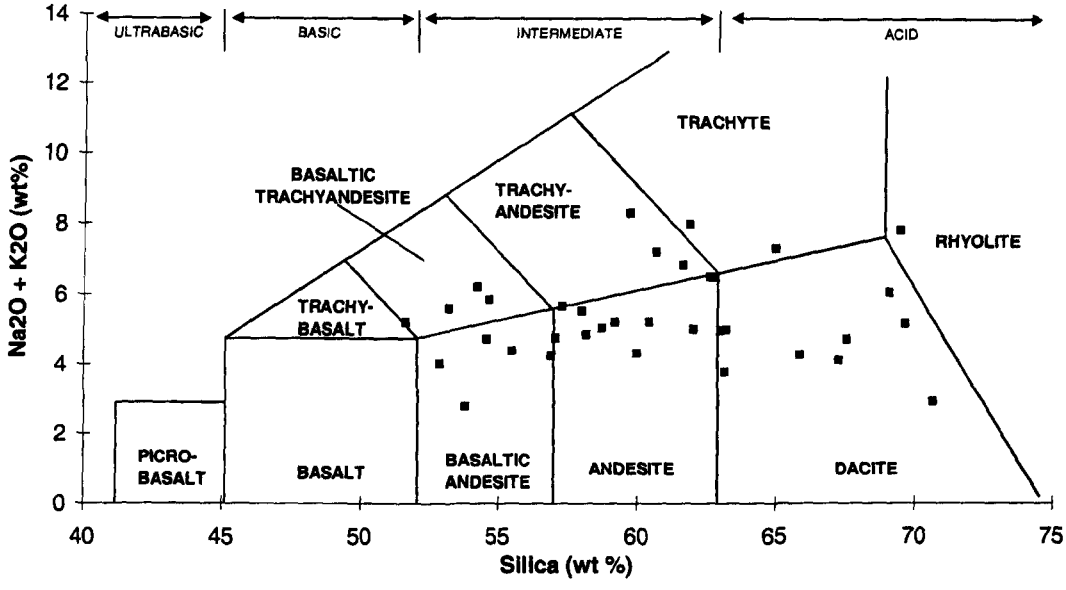
For the purpose of examining the major- (Section 3.3) and trace-element geochemistry (Section 3.4), the rock samples will be considered on the basis of their geological grouping. However, the individual rock types identified during the rock classification exercise will also be used to consider whether different rock types within the geological groups result in different weathering patterns (Section 3.5).

a. Volcanic Rocks

The most common method of determining the rock classification and the nomenclature of volcanic rocks is the total alkalis-silica (TAS) diagram. The sum of Sodium oxide (Na_2O) and Potassium Oxide (K_2O) is calculated from the rock analysis as weight percent (i.e. the total alkali component) and plotted against the Silica content (Figure 3.4). The classification used in the TAS diagram is based on a dataset of 24,000 analyses of fresh volcanic rocks, where the field boundaries denote the minimum amount of overlap between adjoining fields (LeMaitre *et al.*, 1989). The TAS diagram divides rocks into ultrabasic, basic, intermediate and acid on the basis of their silica content. The nomenclature of the classification is based upon a system of root names, which may be subdivided by additional qualifiers (Rollinson, 1993).

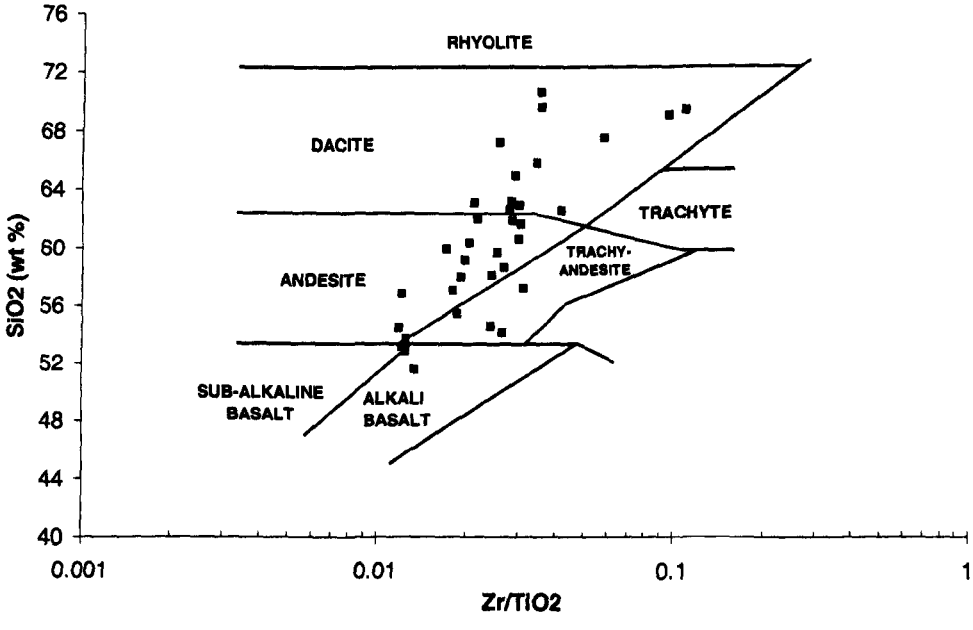
The Borrowdale Volcanics geological unit covers six rock types according to the TAS diagram classification (Figure 3.4). Of the thirty-five volcanic rock samples plotted in Figure 3.4, there are four basaltic andesites, eleven andesites, nine dacites, four basaltic trachyandesites, four trachyandesites, two trachytes and one rhyolite in the study's rock suite. The TAS classification is intended for fresh volcanic rocks, and is not normally appropriate for weathered, altered or metamorphosed rocks because the alkalis are likely to be mobilised.

Figure 3.4. - Chemical classification and nomenclature of volcanic rocks using the total alkalis versus silica (TAS) diagram (After Le Maitre et al., 1989).



Since the Borrowdale Volcanic Group are often highly altered, the TAS classification may be inappropriate and hence it might be preferable to utilise a method of discrimination that uses immobile elements. The classification method of Winchester and Floyd (1977) was used to try to discriminate between the different volcanic rock types of the altered rock samples used in this study (Figure 3.5).

Figure 3.5. - The classification of altered volcanic rock types using Silica versus Zr/TiO_2 diagram (Winchester and Floyd, 1977).

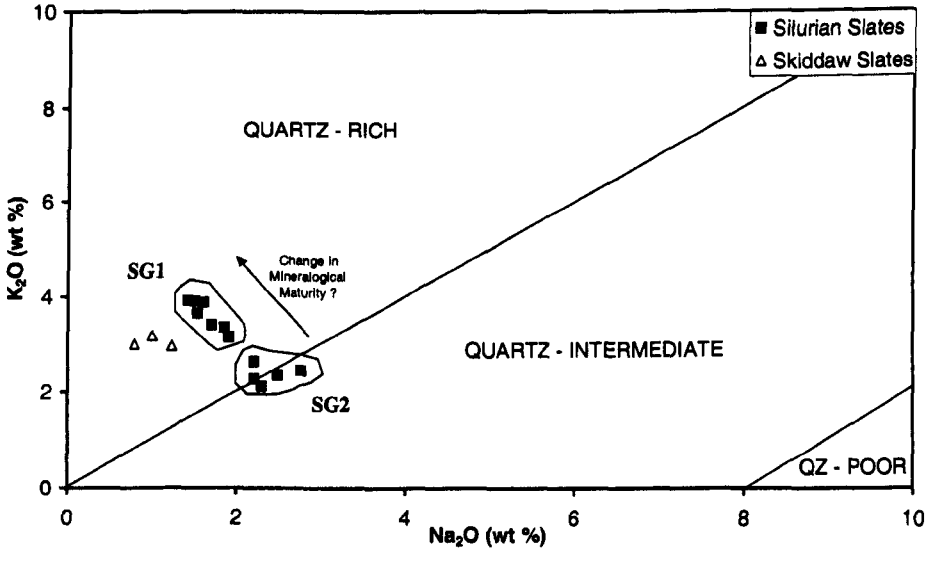


Winchester and Floyd's (1977) rock classification has apportioned the majority of the Borrowdale Volcanic rock samples to two rock types, andesites and dacites; other rock types represent only six of the rock samples. This suggests that the highly altered Borrowdale Volcanic Group is dominated by dacites and andesites, and generally does not incorporate significantly the other four rock types indicated by the TAS classification. Therefore, for the purposes of this study, the six samples from the trachyandesite and alkali basalt groups were incorporated into the andesite group.

b. Sedimentary and Metamorphic rocks

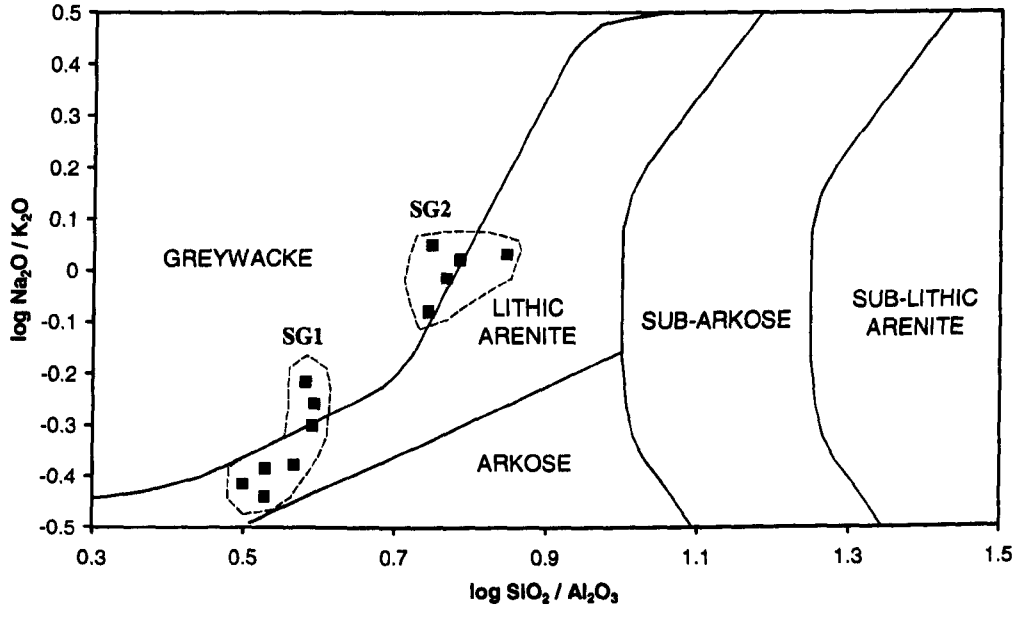
The geochemical classifications of sedimentary and metamorphic rocks are not as developed as the methods used for determining volcanic rocks. Generally, the classification of sedimentary rocks incorporates physical features identified from hand specimens such as grain size, texture and mineralogy (Rollinson, 1993). The most important factor in controlling the geochemical composition of a sedimentary rock is the proportional content of alkalis, particularly sodium and potassium, and alkaline earths, such as calcium and magnesium, in the parent rock. Therefore, basic igneous parent rocks, with abundant calcium and magnesium, are likely to result in smectite clays, whilst granite, rich in alkalis, favours the production of illite (McLane, 1995). The rock samples collected during this study are predominantly greywackes and mudstones. This study utilises three methods of classifying the sediments, (1) Quartz discrimination diagram (Crook, 1974); (2) Log K_2O/Na_2O versus Log SiO_2/Al_2O_3 (Pettijohn *et al.*, 1972); and a ternary diagram plotting ($K_2O + Na_2O + CaO$) versus ($MgO + FeO$) versus Al_2O_3 (Englund and Jorgensen, 1973).

Figure 3.6. - The $K_2O - Na_2O$ diagram used to classify sedimentary rocks proposed by Crook (1974).



The chemical classification of Crook (1974) suggests that the Silurian Slates can be considered as two sub-groups. One of the sub-groups straddles the quartz-rich / quartz-intermediate boundary on the discrimination diagram, whilst the other sub-group is assigned to the quartz-rich section. The Skiddaw Slates are also assigned to the quartz-rich section (Figure 3.6). Sites 6, 20, 21, 22 and 24 straddle the quartz-rich / quartz-intermediate boundary (sub-group 2), whilst sites 3, 4, 5, 10, 16, 17 and 23 fall into the 'quartz-rich' section (sub-group 1). It may be possible that the compositional differences within the Silurian Slate geological group might actually indicate a change in mineralogical maturity (Bhatia, 1983). By way of illustration, the rocks in sub-group 2 on the K_2O – Na_2O diagram will experience an increase in the quartz (silica) content coupled with a concomitant decrease in the proportion of mobile alkali metals over a prolonged period of time. Once this process has occurred, the rocks in sub-group 2 will be located in the same position as sub-group 1 (Figure 3.6). The proportional increase of K_2O, a mobile alkali metal, in sub-group 1 on the K_2O – Na_2O diagram is probably due to the abundance of mica within these more 'mature' rocks.

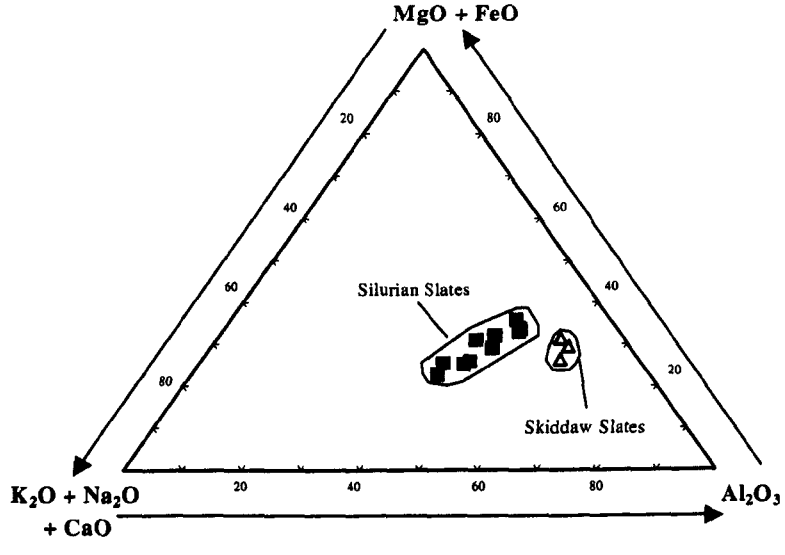
Figure 3.7. - The log K_2O / Na_2O – log SiO_2 / Al_2O_3 diagram used to classify sedimentary rocks proposed by Pettijohn et al. (1972).
NB: Dashed shapes refer to the two sub-groups identified by the K_2O – Na_2O diagram (after Crook, 1974)



The chemical classification of Pettijohn *et al.* (1972) indicates that the Silurian Slates are assigned to two rock types, greywacke and lithic arenite (Figure 3.7). The primary controlling factor in determining the type and geochemistry of a sedimentary rock

is its provenance – i.e. the composition of the source rock and the relief, climate and vegetation of the source terrain. This might suggest that the two sub-groups identified by Crook's classification (Figure 3.6) essentially reflect a change in rock type brought about by variations in provenance, but further examination of the data suggested that the two sub-groups are not divided on the basis of rock type (Figure 3.7). Since the split is independent of rock type, the data may go some way to support the hypothesis of Bhatia (1983) regarding a change in mineralogical maturity. However, Pettijohn *et al.* (1972) themselves admit that the classification is not particularly useful for naming purposes, but is a tool for examining relationships between elemental composition, mineralogy and rock type. The Skiddaw Slates were not included in this classification as the sodium-potassium ratio is likely to be erroneous due to mobilisation of alkalis during metamorphism (Rollinson, 1993).

Figure 3.8. - The (K_2O + Na_2O + CaO) – (MgO + FeO) – Al_2O_3 ternary diagram used to classify sedimentary rocks proposed by Englund & Jorgensen (1973)



The chemical classification of Englund & Jorgensen (1973) also suggests that the Silurian Slates and the Skiddaw Slates are characterised by distinct rock compositions (Figure 3.8). However, the split into two sub-groups of the Silurian Slates group, which was previously identified in Figures 3.6 and 3.7, is not as apparent when the (K_2O + Na_2O + CaO) – (MgO + FeO) – Al_2O_3 classification is used.

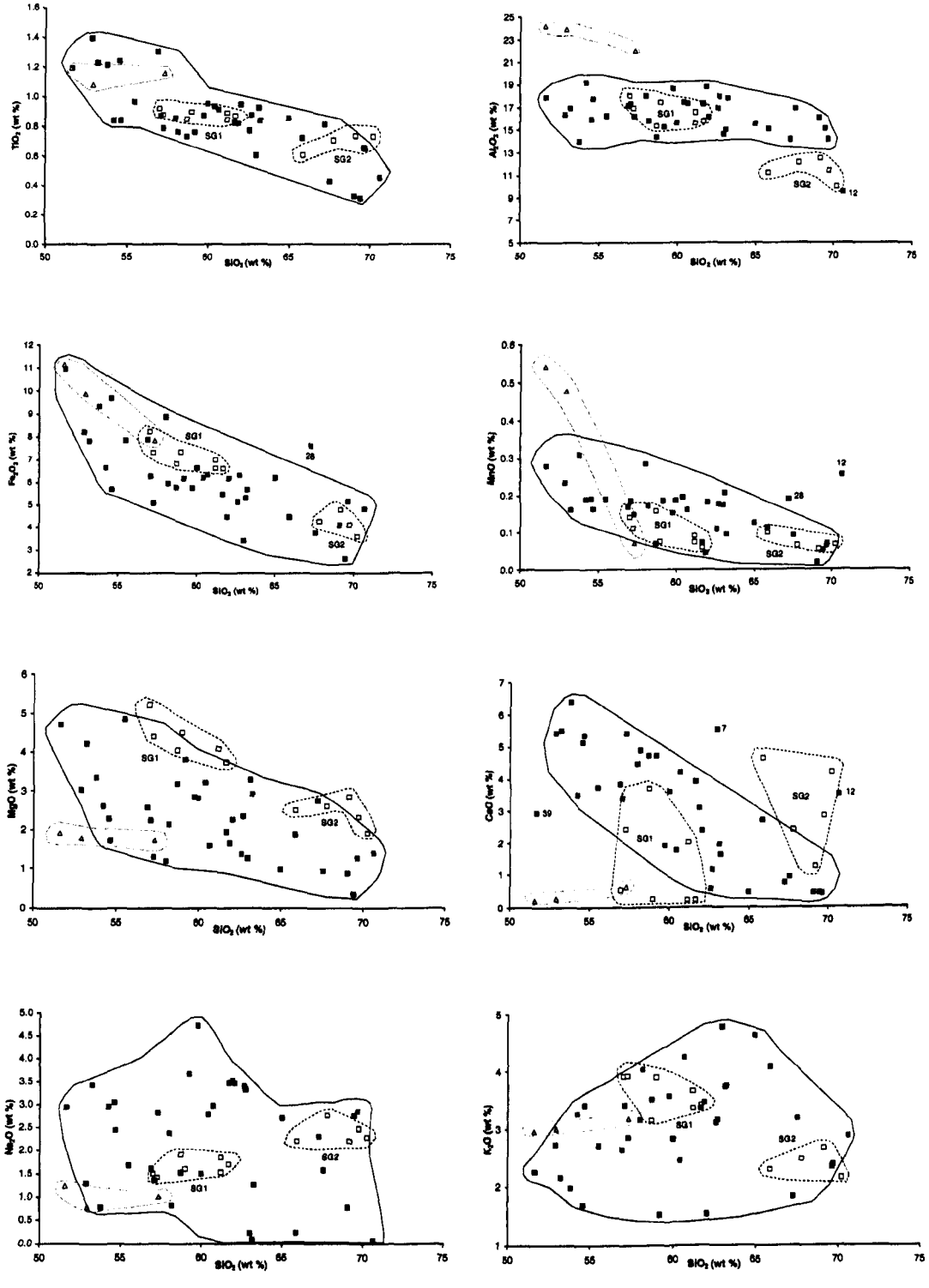
The Silurian Slate samples are assigned to the 40–50 % range on the Al_2O_3 axis, the 25–35 % range on the MgO + FeO axis, and the 15–35 % range on the $K_2O + Na_2O + CaO$ axis. The Skiddaw Slate samples are more homogeneous than the Silurian Slates. The samples are assigned to the 58–60 % range on the Al_2O_3 axis, the 26–31 % range on the MgO + FeO axis, and the 10–13 % range on the $K_2O + Na_2O + CaO$ axis. The much wider range of values on the $K_2O + Na_2O + CaO$ axis in the Silurian Slates group, caused by heterogeneous mobile alkali compositions, may lead to different weathering rates. It is therefore important to examine whether the difference in mobile alkali composition between the two rock types is linked to different weathering patterns. The identification of weathering patterns from the fresh and weathered geochemical data of all the rock samples is fully discussed in Section 3.5.

Despite their simplicity, the classification schemes for volcanic and sedimentary rocks have identified six types of rock in the suite of samples. There are 21 andesites and 14 dacites within the Borrowdale Volcanic Group, 7 greywackes and 5 lithic arenites in the Silurian Slates. In addition, there are 3 metamorphosed Skiddaw Slates and a granite sample. The variation in the geochemical data of these rock types is fully discussed in the next section (Section 3.3.2).

3.3.2. An assessment of rock heterogeneity with variation diagrams

In tabulated form (Appendix E), patterns in the geochemical data are almost impossible to identify. Geologists often use variation diagrams to identify trends within a suite of individual rock samples. On a bivariate variation diagram, the relationship between two elements is examined and this may separate the data into particular geochemical processes. Usually the oxide with the greatest range in composition, which normally is silica, is selected for plotting along the *x*-axis to allow maximum data spread (Rollinson, 1993). The plots, which use silica as a differentiation index on the *x*-axis, are more commonly known as 'Harker diagrams' (Harker, 1909). Harker diagrams are the most frequently used means of displaying major-element data for igneous rocks. In this study, the variation in rock sample composition from all the geological groups was assessed using Harker diagrams (Figure 3.9).

Figure 3.9. - Harker diagrams showing the range of compositions in the Borrowdale Volcanic geological group (n = 35), the Silurian Slate geological group (n = 12) and the Skiddaw Slate geological group (n = 3).
Key:- Borrowdale Volcanics (Filled squares); Silurian Slates (Open squares); Skiddaw Slates (Triangles)



To interpret the volcanic data from the Harker diagrams, the variation of the individual element with silica is assessed and the range of major-element compositions of each rock group are interpreted in terms of mineral fractionation processes. The fields drawn around the data indicate broad trends in the elemental behaviour of the rock groups. However, a closer examination of the data suggested that there are four sites in the Borrowdale Volcanic Group which record unusual compositions for some of the elements. These sites are included in the Harker diagram but are eliminated from the field drawn around the general trend of the Borrowdale Volcanics data (Figure 3.9). In addition, the samples identified as Silurian Slates are considered both as a single geological group and as the two separate sub-groups identified in Section 3.3.1b.

The range in composition, the trends with silica and the fractionation patterns within the transition metals are considered first. The transition metals tend to be less mobile than their alkali metal counterparts (McLane, 1995). Titanium composition exhibits a steep negative trend with silica for the Borrowdale Volcanics (0.4–1.4 wt %), a shallow negative trend for the Silurian Slates (0.6–1 wt %) and no trend for the Skiddaw Slates (1–1.2 wt %). In igneous rocks, titanium partitions into magnetite or ilmenite (metal oxides) during magmagenesis. Magnetite and ilmenite crystallises in the magma chamber and settles to the chamber floor, or pronounced crystallisation along the chamber walls and roof occurs as a response to cooling. During eruption, magma entrains some oxides, however most is left in the magma chamber. Therefore, titanium is lower in the evolved magmas compared to the magmas that have not fractionated magnetite and ilmenite. It is possible that the negative trend between titanium and silica in the Borrowdale Volcanic Group suggests the decreasing titanium composition is due to a progressive increase in mineral fractionation. The trends of the two metasedimentary slate groups require different explanations since the titanium content of slates is a feature of the source region of the sediments. For example, the Silurian Slates may have been derived from the volcanoes that formed the Borrowdale Volcanics and thus titanium is lower in the rocks with high silica due to a different source region. Another possible explanation is that varying amounts of weathering are responsible for the compositional differences.

Aluminium composition exhibits a steep negative trend with silica for the Silurian Slates (9–18 wt %), a shallow negative trend for the Skiddaw Slates (22–25 wt %) and no trend for the Borrowdale Volcanics (14–19 wt %). However, the Borrowdale Volcanics trend might have been interpreted as a shallow negative trend if an outlier (9 wt %) had been considered. Aluminium is often partitioned into plagioclase during magmagenesis. The aluminium composition displays no trend for the Borrowdale Volcanic Group

suggesting that plagioclase may have crystallised but did not fractionate. The observed trend in aluminium in the Silurian Slates is probably the product of weathering from different rock types. The sites with higher aluminium content most likely reflect weathering of an aluminium rich mafic rock, whilst the sites with low aluminium content are possibly the product of a more evolved source rock. Another explanation for the patterns in the Silurian and Skiddaw Slates could be that the negative trend (i.e. from left to right on the diagram) is an index of preferential weathering. However this explanation seems less likely in this case, as aluminium is not usually considered a fluid mobile element.

Iron compositions exhibit steep negative trends with silica for the Borrowdale Volcanics (3–11 wt %), the Silurian Slates (4–8 wt %) and the Skiddaw Slates (8–11 wt %). Iron is often partitioned into clino-pyroxene, which is especially common in basic and intermediate volcanic rocks. Therefore, it is possible to suggest that the negative trend between iron and silica in the mafic rocks (~50–60 wt %) of the Borrowdale Volcanic Group represents a progressive increase in clinopyroxene fractionation, whereas the iron composition above ~62 wt % silica shows a greater degree of scatter. The difference in the iron composition of the slate groups is again probably due to a different source rock or weathering processes.

Manganese composition exhibits a steep negative trend with silica for the Skiddaw Slates (0–0.6 wt %), and a shallow negative trend to no trend for the Borrowdale Volcanics (0–0.3 wt %) and the Silurian Slates (0–0.2 wt %). Manganese is often partitioned into magnetite. Therefore, the negative trend between manganese and silica in the Borrowdale Volcanic Group represents a progressive increase in magnetite fractionation, with increasing silica content of the rock. During metamorphism, it is possible that a differing amount of fractionation can occur in rocks of the same type. Therefore, it is possible to suggest that the strong negative trend between manganese and silica in the Skiddaw Slate group is caused by differing degrees of metamorphism experienced in the localities where the individual samples were collected. Again, the shallow negative trend in the Silurian Slates is probably due to differences in source rock composition or weathering processes.

The alkali metals tend to have higher levels, larger data spreads and less prominent trends within the data than the transition metals. Magnesium composition exhibits a steep negative trend with silica for the Borrowdale Volcanics (0–5 wt %) and the Silurian Slates (2–5 wt %) and no trend for the Skiddaw Slates (all values are circa 2 wt %). Magnesium partitions into pyroxene, which is especially common in basic and intermediate volcanic rocks. Therefore, it is possible that the negative trend between magnesium and silica in the Borrowdale Volcanic Group suggests the decreasing magnesium composition is due to a

progressive increase in pyroxene fractionation. The negative trend in the Silurian Slates is probably due to differences in source rock composition or weathering processes.

Calcium exhibits a steep negative trend with silica for the Borrowdale Volcanics (0–6 wt %) and no trend for the Silurian Slates (0–5 wt %) and the Skiddaw Slates (all values less than 1 wt %). Calcium is fluid mobile, which accounts for the equidistant data distribution and the lack of any real prominent trends between calcium and silica in the Silurian and Skiddaw Slate groups. In volcanic rocks, calcium partitions into calcic-plagioclase (i.e. anorthite) and calcic-pyroxene (i.e. augite). The negative trend between calcium and silica in the Borrowdale Volcanic Group is probably due to augite fractional crystallisation rather than plagioclase in this case. If crystallisation into calcic-plagioclase had taken place, then a concomitant decrease in aluminium and sodium would also have occurred, but was not been observed here.

Sodium composition exhibits no trend with silica for the Silurian Slates (1.5–2.5 wt %), the Borrowdale Volcanics (0–5 wt %) and the Skiddaw Slates (all values circa 1 wt %). Sodium is fluid mobile, which accounts for the equidistant data distribution and the lack of any real prominent trends between sodium and silica in the Borrowdale Volcanic Group and the Silurian and Skiddaw Slate groups.

Potassium composition exhibit a steep negative trend with silica for the Silurian Slates (2–4 wt %) and no trend for the Borrowdale Volcanics (0–5 wt %) and the Skiddaw Slates (all values circa 3 wt %). Potassium often partitions into biotite or alkali feldspar. A possible explanation for the negative trend in the Silurian Slates group is that the lower silica Silurian Slates have a higher biotite content than the higher silica Silurian Slates, in which more felsic phases may dominate. The equidistant data distribution and the lack of any real prominent trends between potassium and silica in the Borrowdale Volcanic Group and the Skiddaw Slates may be a result of potassium's fluid mobile nature.

The examination of the Harker diagrams suggests that the Silurian Slates are apportioned into two distinct sub-groups, as already identified by the classification exercise (Section 3.3.1.b). Sub-group 1 has lower silica (57–62 wt % vs 66–70 wt %) and sodium (1.5–2 wt % vs 2–2.5 wt %) compositions than sub-group 2 (Figure 3.9). Sub-group 1 also has higher levels of titanium (0.8–1 wt % vs 0.6–0.8 wt %), aluminium (15-18 wt % vs 9-13 wt %), magnesium (4–5 wt % vs 2–3 wt %) and potassium (3–4 wt % vs 2–2.5 wt %) than sub-group 2. The first sub-group has negative trends with titanium, aluminium, iron, manganese, magnesium and potassium, and no trends with calcium and sodium. The second sub-group has negative trends with aluminium, iron, magnesium and potassium, no trends with manganese, calcium and sodium, and a positive trend with titanium.

Since the mineralogical maturity hypothesis seems the most plausible explanation for differences in the geochemical composition of the two Silurian Slate sub-groups, the former weathering conditions were examined using the method of Nesbitt and Young (1984, 1989). The former weathering conditions in the suite of Silurian Slates was found by plotting the major-element data on a ($CaO + Na_2O$) – Al_2O_3 – K_2O triangular diagram (Figure 3.10).

Figure 3.10 - $CaO + Na_2O - Al_2O_3 - K_2O$ diagram (Nesbitt and Young, 1984, 1989) showing the compositions of the Silurian Slate sub-groups (1 = Low SiO_2 sub-group, 2 = High SiO_2 sub-group).
N.B. The weathering trend and advanced weathering trends are also shown, as are the compositions of plagioclase (P), K-Feldspar (KF), muscovite (M), Illite (I), Smectite (S) and kaolinite (K) for reference purposes.

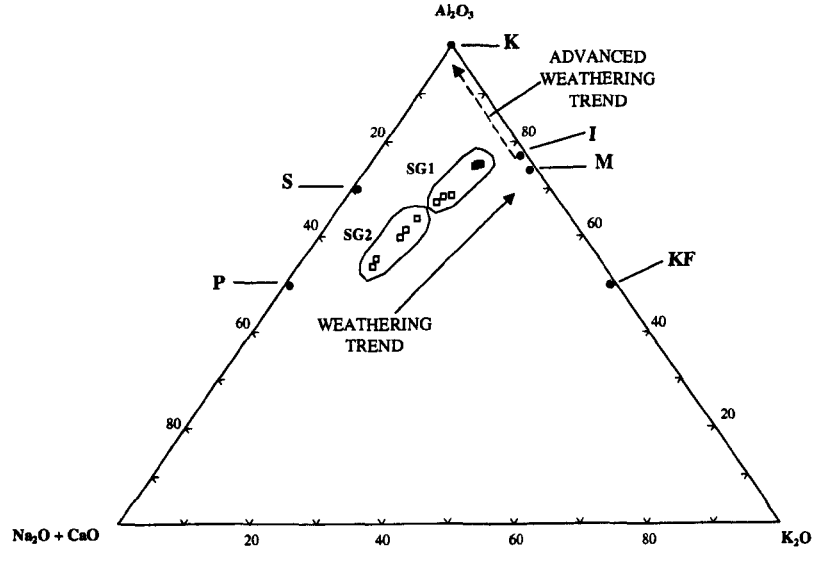


Figure 3.10 suggests that the Silurian Slate data plots along the weathering trendline identified by Nesbitt and Young (1984, 1989). This suggests that the chemical change that has occurred in the Silurian Slates is attributable to the movement along the weathering line towards mineralogical maturity (c.f. Bhatia, 1983). The examination of the ternary diagram suggests that sub-group 1 has passed through the weathering processes, and associated geochemical changes, currently being experienced by sub-group 2.

In summary, the examination of the major-element geochemistry has found that the rock samples are variable both within the suite of samples and between the geological groups. The Borrowdale Volcanic Group displays a large range in composition, it varies

from ~51 wt % to ~70 wt % silica, accompanied by a concomitant variation in the composition of the transition and alkali metals. The Silurian Slates have two distinct sub-groups. Sub-group 1 with ~57–62 wt % silica, has higher levels of all the metals, with the exception of sodium. The constant sum rule (i.e. sum of ions always equals 100 %) means that although the silica compositions of sub-group 2 (~66–70 wt %) are significantly higher than sub-group 1, the transition and alkali metals have to record significantly lower compositions to add up to 100 %. The Skiddaw Slates have a much more homogeneous composition than the other two geological groups with silica compositions varying from ~51–57 wt %. The Skiddaw Slate transition metal composition has a larger data spread than the alkali metals, which are almost completely homogeneous.

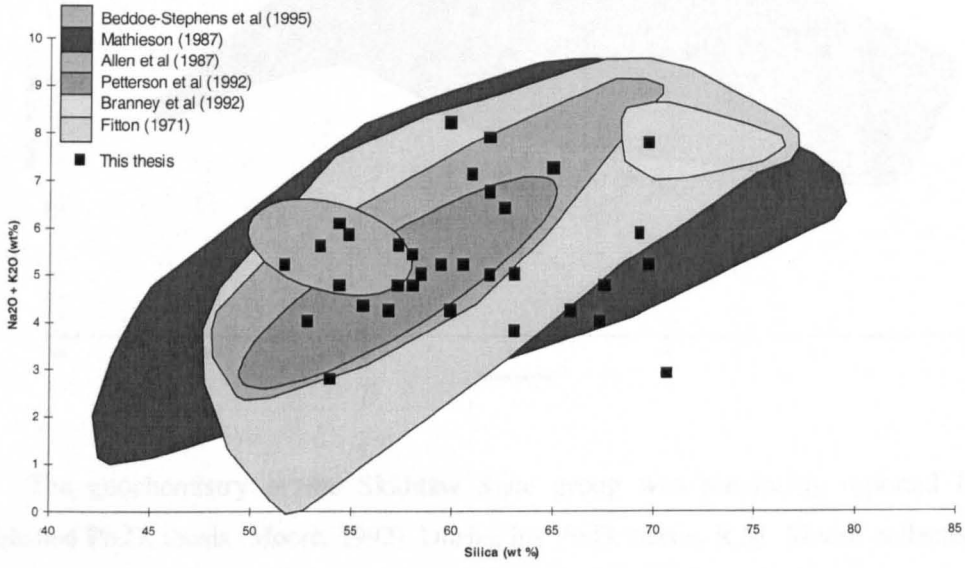
"The constant sum rule has been a headache for statisticians who for a very long time have been informing geologists that they are working in a minefield of spurious correlations and unsound interpretations" (Rollinson, 1993). Therefore, a much sounder technique is the use of trace elements, in association with interpretations from major-element geochemistry, to identify the processes associated with rock composition differences. Thus, when analysing complex geochemical data geologists commonly use trace elements (Section 3.4).

3.3.3. Comparing the present Lake District results with previous work

Several studies have previously examined whole rock chemistry of the three Lake District geological groups. To put the present work in context, a short description of these "historical" studies follows, and the major-element data are compared with the data from the current study.

There are 6 previous studies with Borrowdale Volcanics incorporating major and trace element data covering the majority of the volcanic rock spectrum from basic (i.e. basalts) to acidic rocks (i.e. rhyolites). J.G. Fitton analysed 165 samples (Fitton, 1971) and N.A. Mathieson analysed a further 117 samples (Mathieson, 1987) over the whole Borrowdale Volcanic Group during their Ph.D. theses. In addition, in the west of the Borrowdale Volcanic Group, further studies analysed 48 (Allen *et al.*, 1987), 11 (Petterson *et al.*, 1992) and 29 samples (Beddoe-Stephens *et al.*, 1995) respectively. M.J. Branney analysed a further 18 samples from the Bad Step Tuff (central Borrowdale Volcanics) during his Ph.D. thesis (Branney, 1988) and a subsequent publication (Branney *et al.*, 1992). The rock compositions from each of the studies were compared with the current study using a total alkali-silica diagram (Figure 3.11).

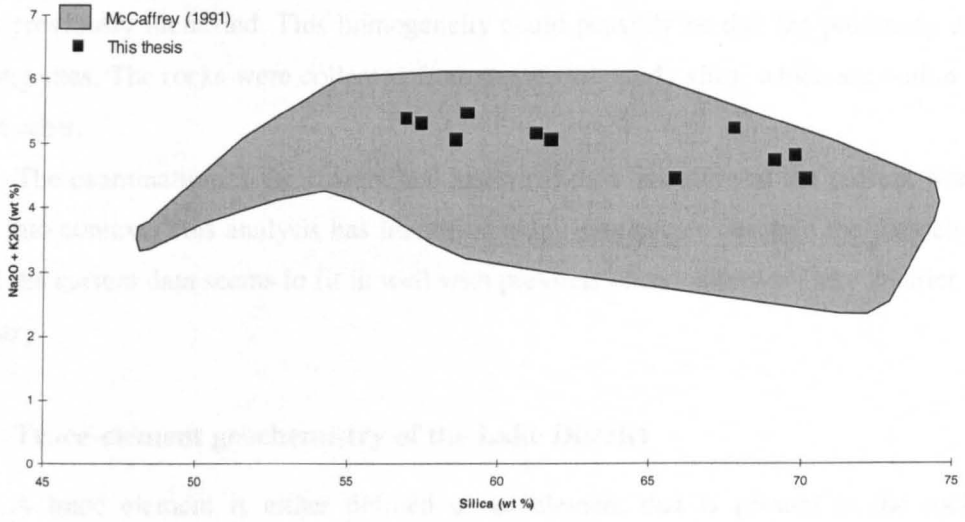
Figure 3.11 - Current data from rock samples of the Borrowdale Volcanic Group compared with data from previous studies.



In general, the rock samples of the Borrowdale Volcanic group from this study are in good agreement with data from previous work. The ranges in total alkalis and silica composition are slightly smaller than found by the previously published studies, but on the whole the data are comparable. Using composition fields may introduce bias because it only requires one site to have above average or below average concentrations to extend the field, but further examination of the data suggested this was not the case here.

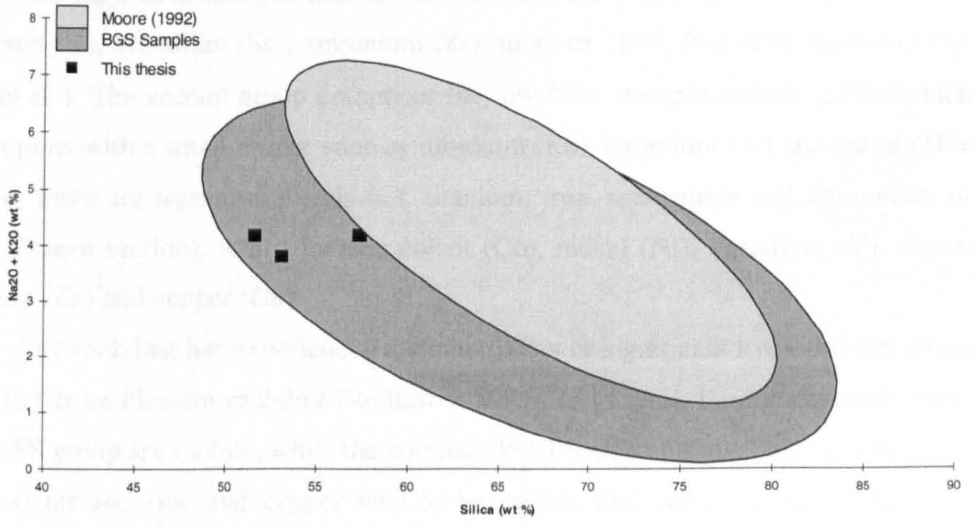
The geochemistry of the Silurian Slates was previously reported by an unpublished Ph.D thesis (McCaffrey, 1991). W.D. McCaffrey analysed 54 samples over the whole of the Silurian Slates during his Ph.D. thesis. The rock compositions from McCaffrey's thesis were compared with the current study using a total alkali-silica diagram (Figure 3.12). In general, the current study seems to be in good agreement with McCaffrey's data, but tends to have a smaller total alkali and silica range.

Figure 3.12 - Current data from rock samples of the Silurian Slates compared with data from previous studies.



The geochemistry of the Skiddaw Slate group was previously reported by an unpublished Ph.D. thesis (Moore, 1992). During his Ph.D. thesis, R.M. Moore collected and analysed 26 samples from the Skiddaw Slates, and he compared his data with a further 71 samples provided by the British Geological Survey. The rock compositions from Moore's thesis and the BGS samples were compared with the current study using a total alkali-silica diagram (Figure 3.13).

Figure 3.13 - Current data from rock samples of the Skiddaw Slates compared with data from previous studies.



The data in the current study falls within the fields drawn from published data (Moore, 1992). However, the data in this study is considerably more homogeneous than the ranges previously identified. This homogeneity could possibly be due the proximity of the sampling sites. The rocks were collected from the stream study sites, which are within 5km of each other.

The examination of the current and historical data has allowed the present work to be put into context. This analysis has identified many similarities between the datasets and overall the current data seems to fit in well with previous observations of Lake District rock chemistry.

3.4. Trace-element geochemistry of the Lake District

A trace element is either defined as an element that is present in the rock in concentrations of less than 0.1 weight percent, or alternatively in concentrations less than 1000 parts per million (Rollinson, 1993). Trace element abundances were determined by XRF analysis. The analytical techniques and data tables are given in Appendix B and Appendix E, respectively.

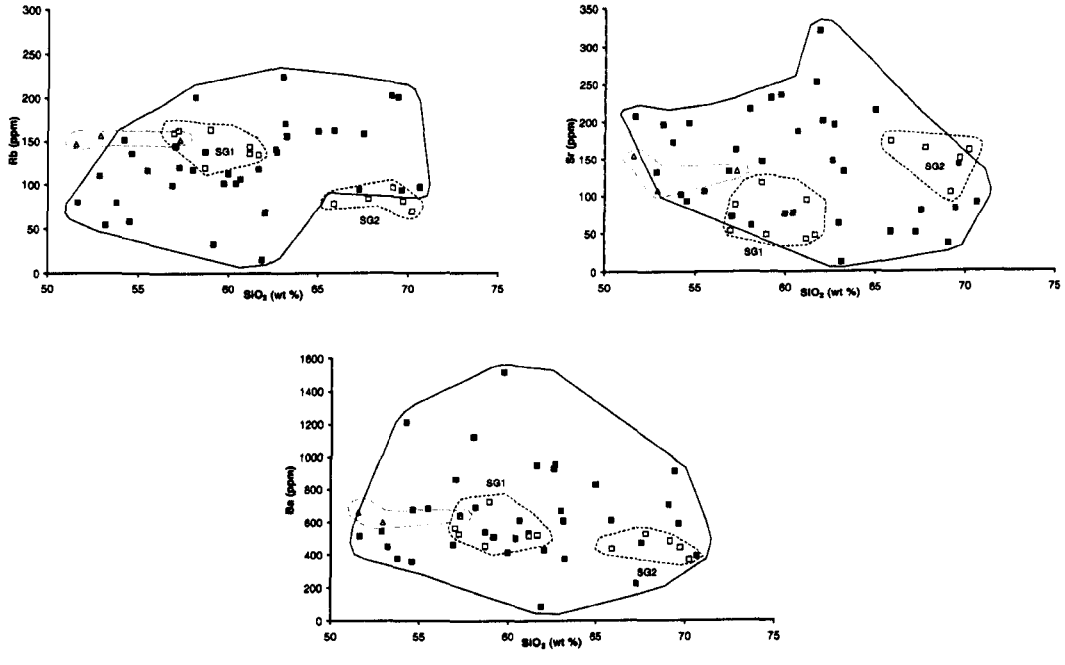
In magmatic systems, trace elements either have a preference for the solid phase in the form of minerals (compatible elements) or they will partition strongly into the melt phase (incompatible elements). For this reason, trace elements are often classified by their behaviour in magmatic systems, or less frequently, by their position on the periodic table (Rollinson, 1993). The trace elements essentially split into three groups, which are considered as separate fields during the examination of the rock geochemistry. The first group is the high field strength cations (HFS), which are small highly charged cations such as yttrium (Y), scandium (Sc), zirconium (Zr), niobium (Nb), lead (Pb), thorium (Th) and uranium (U). The second group comprises the low field strength cations (LFS), which are large cations with a small charge such as rubidium (Rb), strontium (Sr) and barium (Ba). In addition, there are transition metals (c.f. titanium, iron, manganese and aluminium in the major-element section), which include cobalt (Co), nickel (Ni), vanadium (V), chromium (Cr), zinc (Zn) and copper (Cu).

Any rock that has experienced metamorphism or significant hydrothermal alteration will suffer from element mobility (Rollinson, 1993). In general, the incompatible elements in the LFS group are mobile, while the compatible HFS elements are fluid immobile. Of the transition metals, zinc and copper tend to be mobile and cobalt, nickel, vanadium and chromium are immobile.

3.4.1. An assessment of rock heterogeneity with variation diagrams

As for major-element analysis, the trends in the rock suite are assessed using silica on the *x*-axis to allow maximum data spread. The trace-element abundances from all geological groups in the rock suite were also assessed using Harker diagrams. The trace-element data was examined using the three groups previously identified, i.e. the LFS group, the HFS group and the transition metals group. As with the major elements, the fields drawn around the data indicate broad trends in the elemental behaviour of the rock groups.

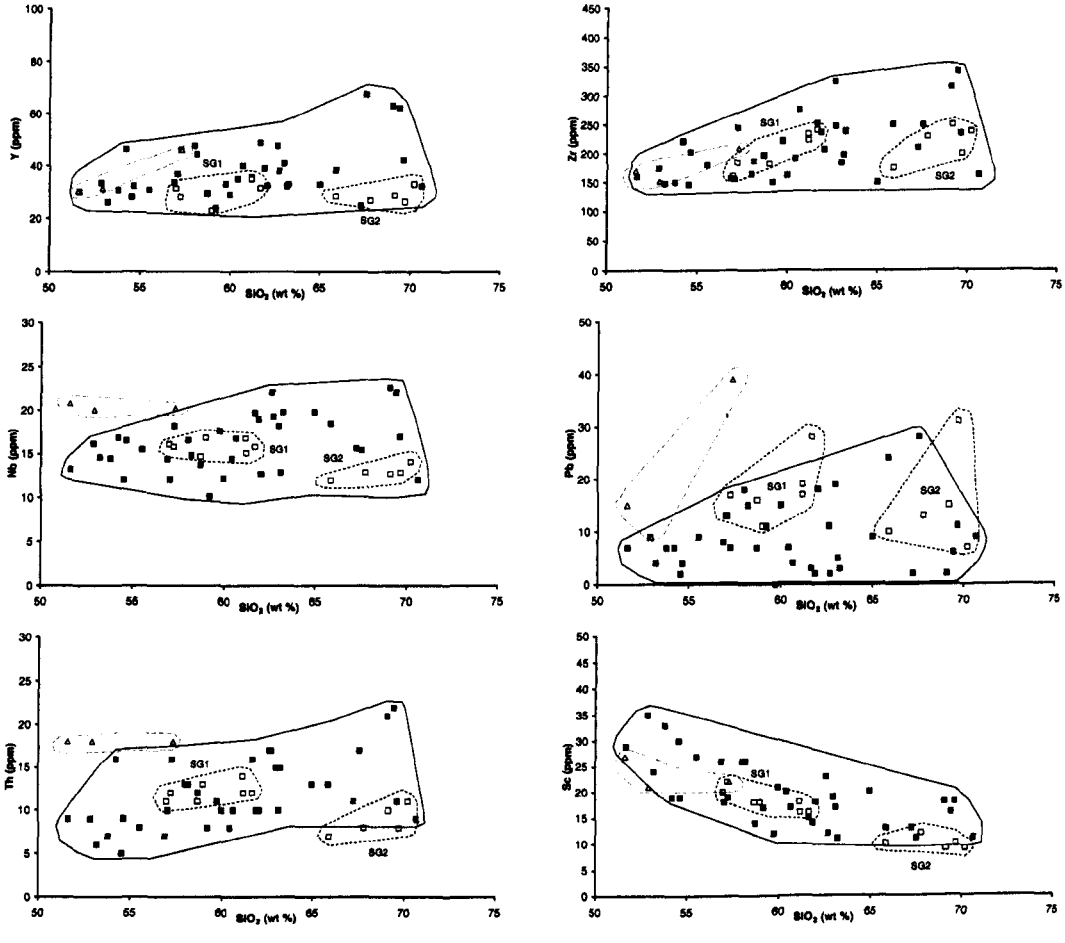
Figure 3.14 - Harker diagrams showing the range of abundances in the Borrowdale Volcanic Group (n = 35), the Silurian Slates (n = 12) and the Skiddaw Slates (n = 3) for the LFS group.
Key:- Borrowdale Volcanics (Filled squares); Silurian Slates (Open squares); Skiddaw Slates (Triangles)



The range in composition and the trends with silica within the low field strength (LFS) group are considered first (Figure 3.14). Rubidium concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (15–225 ppm), the Silurian Slates (69–164 ppm) and the Skiddaw Slates (147–156 ppm). Strontium concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (13–322 ppm) and the Skiddaw Slates (107–154 ppm), and a shallow positive trend with silica in the Silurian Slates (43–174 ppm). Barium concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (88–

1214 ppm), the Silurian Slates (367–728 ppm) and the Skiddaw Slates (599–661 ppm). As we have already established (Section 3.4), rubidium, strontium and barium are all fluid mobile elements and a closer examination of Figure 3.14 suggests that the Borrowdale Volcanic Group exhibits a large data spread and lacks any prominent trends between these three elements and silica. Although the Silurian and Skiddaw Slates exhibit a smaller data spread in these elements, they also lack any discernible trends. Therefore, the non-conservative behaviour of the elements in the LFS group are reflected by a large data spread and a lack of patterns in all rock types.

Figure 3.15 - Harker diagrams showing the range of abundances in the Borrowdale Volcanic Group (n = 35), the Silurian Slates (n = 12) and the Skiddaw Slates (n = 3) for the HFS group.
Key:- Borrowdale Volcanics (Filled squares); Silurian Slates (Open squares); Skiddaw Slates (Triangles)



The range in composition and the trends with silica within the high field strength (HFS) group are considered in Figure 3.15. Yttrium concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (25–68 ppm) and the Silurian Slates (23–36

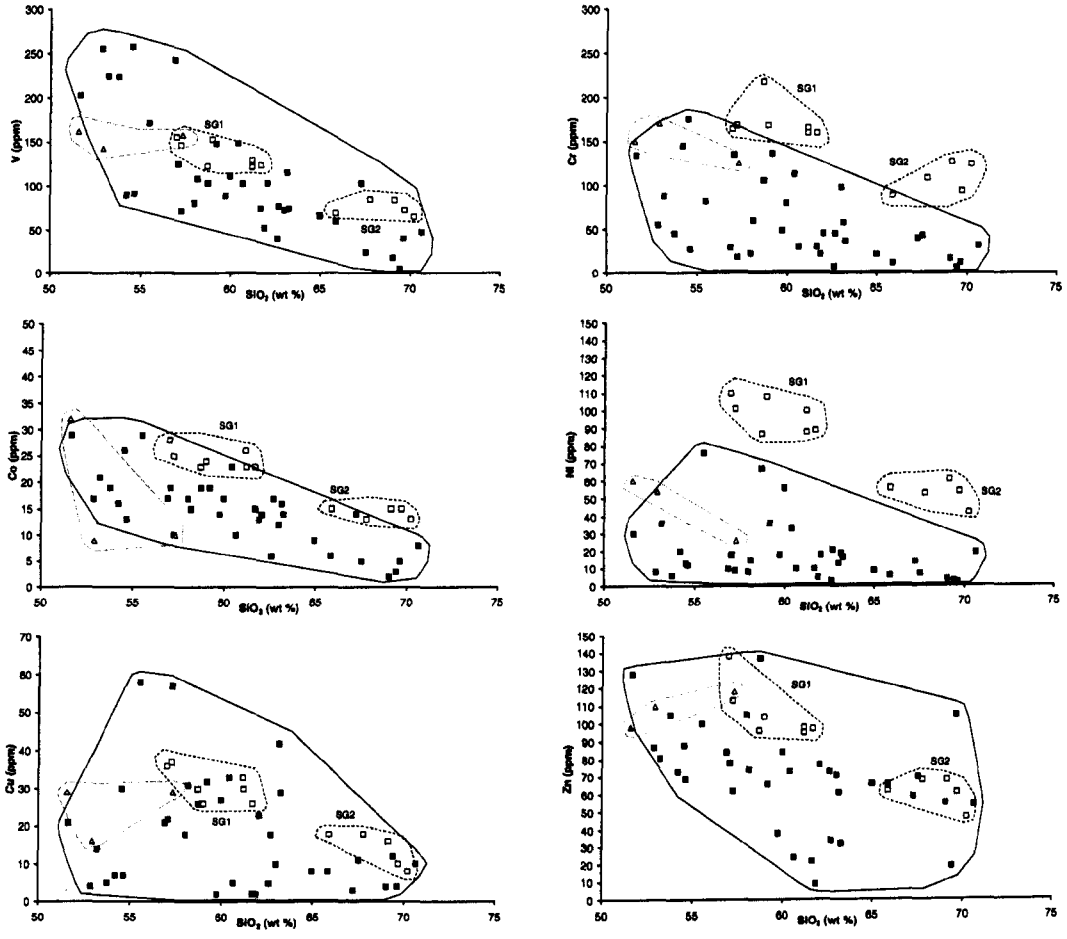
ppm), and a shallow positive trend in the Skiddaw Slates (30–46 ppm). Zirconium concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (146–342 ppm), the Silurian Slates (161–382 ppm) and the Skiddaw Slates (152–209 ppm). Niobium concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (10–23 ppm), the Silurian Slates (12–17 ppm) and the Skiddaw Slates (20–21 ppm). Lead concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (0–28 ppm), the Silurian Slates (7–31 ppm) and the Skiddaw Slates (9–39 ppm). Thorium concentrations exhibit no trend with silica for the Borrowdale Volcanic Group (5–22 ppm), the Silurian Slates (7–14 ppm) and the Skiddaw Slates (18 ppm).

Yttrium, zirconium, niobium, lead and thorium are largely incompatible and should all increase with increasing silica during crystal fractionation. However, the generally flat trends indicated by the Borrowdale Volcanic Group may result from HFS element mobility during metamorphism. This may also be true for the slate samples, although in these rocks varying sedimentary sources will contribute to the 'noise'.

In contrast, scandium concentrations exhibit negative trends with silica for the Borrowdale Volcanic Group (11–35 ppm) and the Silurian Slate (9–22 ppm), and no trend in the Skiddaw Slates (21–27 ppm). Scandium is often partitioned into magnetite and pyroxene during magmagenesis. Therefore, the negative trend between scandium and silica in the Borrowdale Volcanic Group may suggest that decreasing scandium concentrations are due to a progressive increase in magnetite or pyroxene fractionation. The scandium content of slates is an artefact of the source region of the sediments. This suggests that the low silica, high scandium Silurian Slate samples may have been derived from the volcanics from the Borrowdale Volcanic Group and the high silica samples, which have lower scandium, may be the result of a different source region. Alternatively, they could be the result of differing weathering processes.

The range in composition and the trends with silica within the transition metals group are considered in Figure 3.16. Vanadium concentrations exhibit negative trends with silica for the Borrowdale Volcanic Group (5–258 ppm) and the Silurian Slates (65–156 ppm), and no trend in the Skiddaw Slates (143–162 ppm). Vanadium partitions into magnetite during magmagenesis. Therefore, the negative trend between vanadium and silica in the Borrowdale Volcanic Group may suggest that decreasing vanadium concentrations result from a progressive increase in magnetite fractionation. The negative trend in the Silurian Slates is probably due to differences in source rock composition or weathering processes.

Figure 3.16 - Harker diagrams showing the range of abundances in the Borrowdale Volcanic Group (n = 35), the Silurian Slates (n = 12) and the Skiddaw Slates (n = 3) for the transition metals.
Key:- Borrowdale Volcanics (Filled squares); Silurian Slates (Open squares); Skiddaw Slates (Triangles)



Chromium concentrations exhibit shallow negative trends with silica for the Borrowdale Volcanic Group (6–175 ppm), the Silurian Slates (89–218 ppm) and the Skiddaw Slates (125–170 ppm). Cobalt concentrations exhibit shallow negative trends with silica for the Borrowdale Volcanic Group (2–29 ppm) and the Silurian Slates (13–28 ppm), and a steep negative trend with silica for the Skiddaw Slates (9–32 ppm). Nickel concentrations exhibit shallow negative trends with silica for the Borrowdale Volcanic Group (2–76 ppm), the Silurian Slates (42–110 ppm) and the Skiddaw Slates (26–60 ppm). Chromium, cobalt and nickel partition into magnetite and pyroxene during magmagenesis. Therefore, the negative trend between these three elements and silica in the Borrowdale Volcanic Group may suggest that decreasing chromium, cobalt and nickel concentrations result from a progressive increase in magnetite or pyroxene fractionation. The negative

trends in the Silurian Slates are probably due to differences in source rock composition or weathering processes.

Copper concentrations exhibit a shallow negative trend with silica for the Silurian Slates (8–37 ppm) and no trend for the Borrowdale Volcanic Group (2–58 ppm) and the Skiddaw Slates (16–29 ppm). Zinc concentrations exhibit a shallow negative trend with silica for the Silurian Slates (47–138 ppm), no trend with silica for the Borrowdale Volcanic Group (9–137 ppm), and a shallow positive trend with silica for the Skiddaw Slates (98–118 ppm). Both copper and zinc are fluid mobile, which may explain the considerable data spread and lack any prominent trends in the Borrowdale Volcanic Group and the Skiddaw Slates. In contrast, the Silurian Slates exhibit stronger trends with these two elements. This may be the result of differences in source rock composition or alternatively differing weathering processes.

In summary, the trace-element geochemistry suggests that the rock samples are very variable within the suite of samples as well as between the geological groups. As with the major-element geochemistry, the Borrowdale Volcanic Group is the most heterogeneous group and displays large ranges in most of the element diagrams. Again, the Silurian Slates splits into two distinct sub-groups. Sub-group 1 (~57–62 wt % silica) has higher concentrations of the transitional metals than sub-group 2 (~66–70 wt % silica). In contrast, the concentrations of the HFS and LFS groups are very similar in both sub-groups. The Skiddaw Slates have a much more homogeneous composition than the other two geological groups, but this is to be expected because of the small number of samples in this survey group.

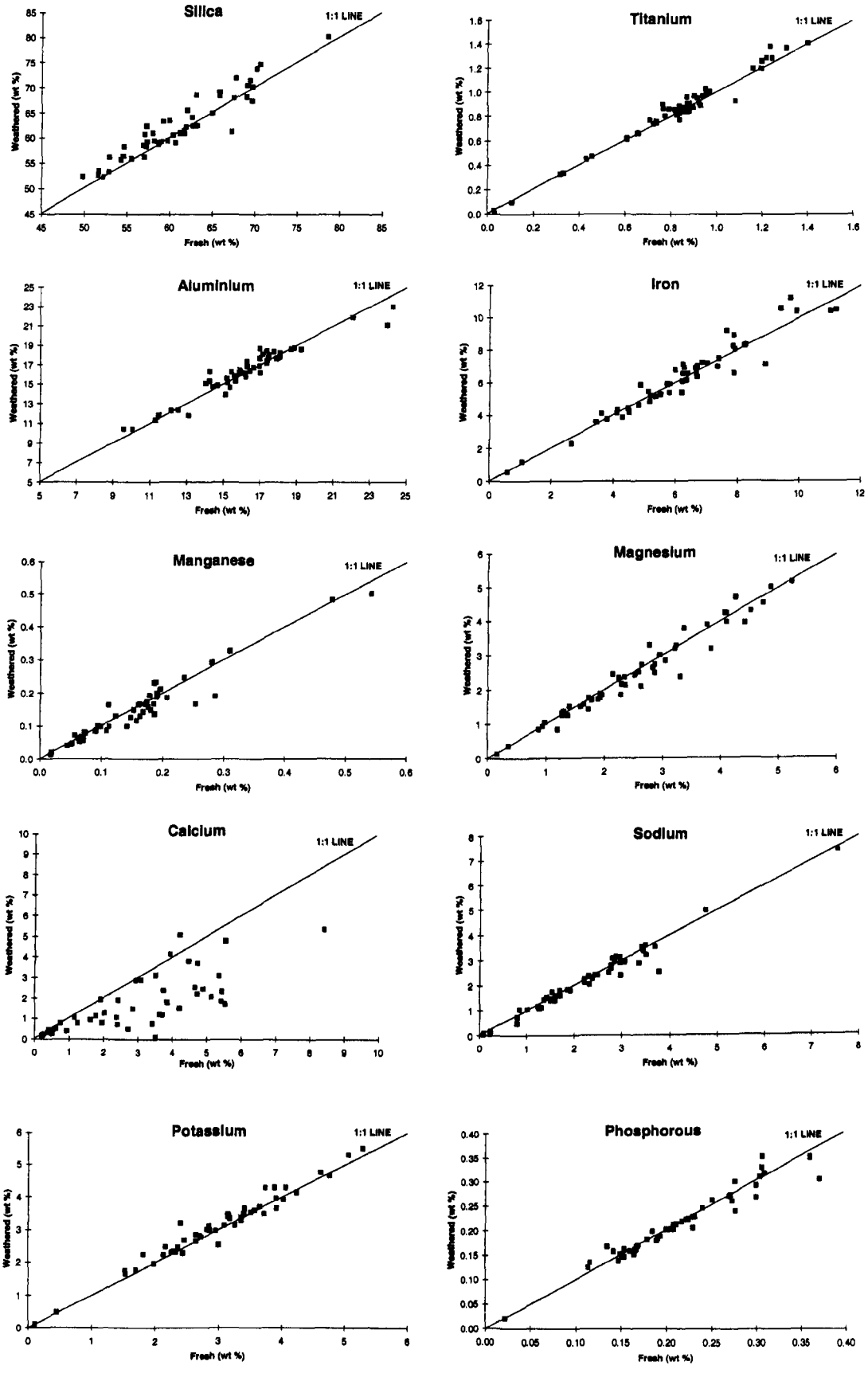
3.5. Attempting to establish weathering patterns from fresh and weathered geochemical data

The next phase of the whole rock chemistry aspect of the thesis involved an attempt to establish weathering patterns from the geochemical data. To achieve this, data obtained by XRF analysis for the weathered and fresh fractions of the rock samples were used. The first step is to determine which elements behave conservatively during weathering.

3.5.1. Major-element behaviour in fresh and weathered rock samples

To establish which major elements were behaving conservatively and which major elements were behaving non-conservatively, the rock samples' weathered composition was plotted against the rock samples' fresh composition (Figure 3.17).

Figure 3.17 - Establishing the behaviour of the major elements during weathering.



It can be clearly identified from Figures 3.17 that some major elements lie on the 1:1 line (i.e. they are behaving conservatively), whilst others are either above or below the line (i.e. they are behaving non-conservatively).

The majority of the silica, titanium, aluminium and potassium values lie above the 1:1 line (upto maximum increases of 5, 0.1, 2 and 1 wt % respectively). This suggests that the rocks are undergoing elemental enrichment during the weathering process (i.e. non-conservative behaviour). Whereas, the iron, manganese, magnesium, sodium and phosphorous values, on the whole, seem to straddle the 1:1 line (± 2, 0.1, 1, 0.5 and 0.05 wt % respectively). This suggests that some sites are experiencing elemental enrichment during the weathering process while others are experiencing elemental depletion. The most prominent trend can be found in the calcium content of the weathered rock samples. All but two of the calcium values lie below the 1:1 line (upto a maximum decrease of 5 wt %), which suggests that the rocks are undergoing elemental depletion during weathering. Calcium is fluid mobile, which accounts for its clear depletion in the weathered rock samples, where almost all calcium is lost in some cases.

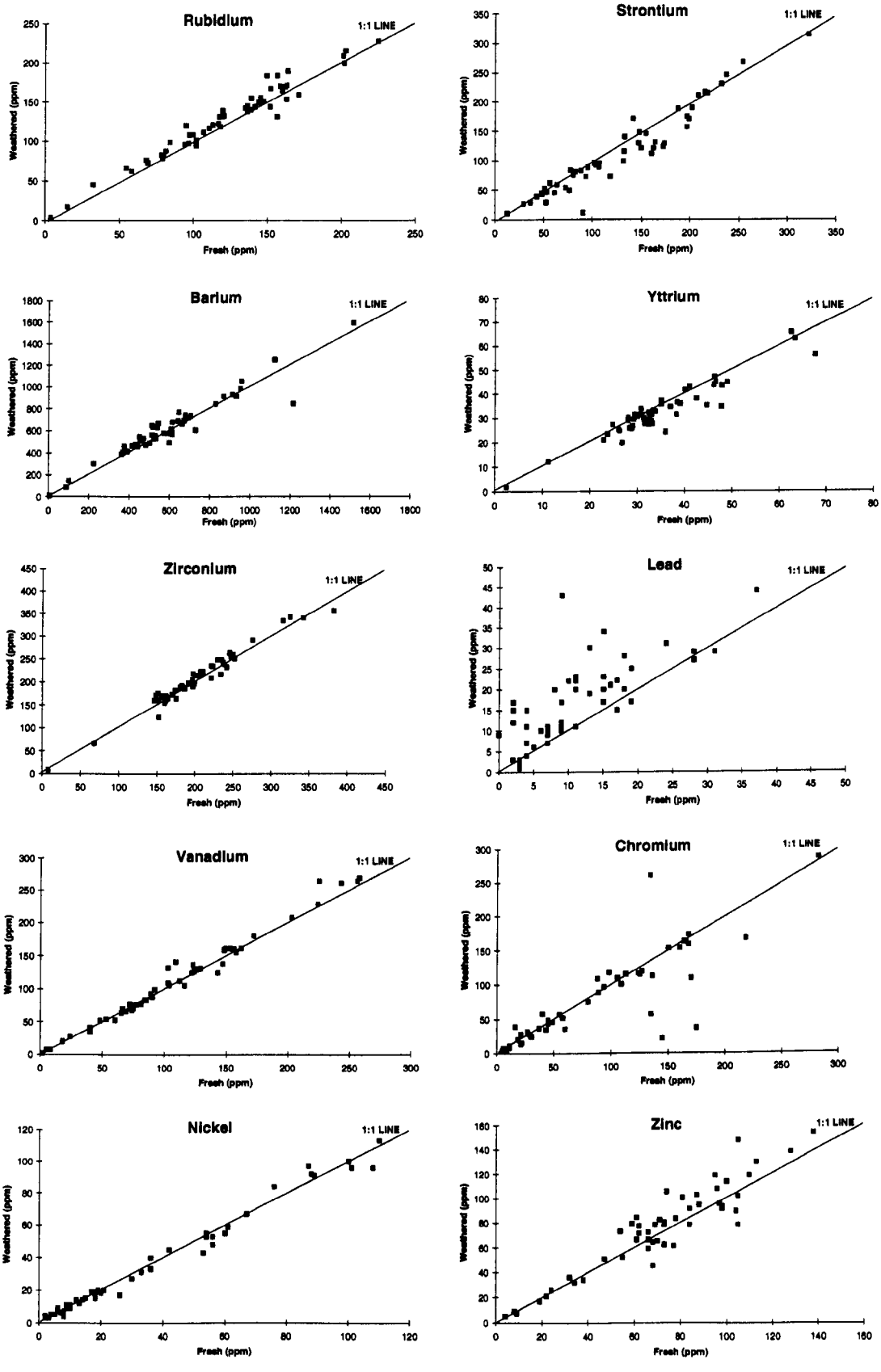
The majority of element values, with the exception of calcium, lie just above the 1:1 line. This does not necessarily suggest that the rock samples have been relatively enriched in these elements during the weathering process due to the constant sum problem. Since the calcium content of the rock samples is clearly depleted significantly during weathering, a concomitant increase in the other elements is a necessary consequence to accommodate for this loss. This does not therefore imply mobility during weathering.

3.5.2. Trace-element behaviour in fresh and weathered rock samples

A similar plot has been undertaken to establish which trace elements behave conservatively during weathering (Figure 3.18). It can be clearly identified from Figure 3.18 that the majority of the trace elements lie on the 1:1 line (i.e. behaving conservatively), whilst a few others are either above or below the line (i.e. behaving non-conservatively).

The majority of the rubidium, barium, zirconium and lead values lie above the 1:1 lines (up to maximum increases of 25, 100, 25 and 35 ppm respectively). There are two possible explanations: a) the rocks may be undergoing elemental enrichment during the weathering process; or b) the concentrations are an artefact of mobile element depletion. The strontium and yttrium values lie below the 1:1 line (up to a maximum decrease of 100 and 20 ppm respectively). This suggests that the rocks are undergoing elemental depletion during weathering. The vanadium, chromium, nickel and zinc values seem to straddle the 1:1 line (± 25, 150, 20 and 40 ppm respectively), suggesting immobile behaviour.

Figure 3.18 - Establishing the behaviour of the trace elements during weathering.



It is possible to suggest from Figure 3.18 that the most prominent depletion trend is to be found in the strontium content of the rock samples. Strontium is fluid mobile, which accounts for its clear depletion in the weathered rock samples, where almost all the strontium is lost in some cases. Strontium and calcium seem to have similar patterns in the major and trace element 1:1 lines. This is unsurprising since the two elements have the same charge and similar ionic radius and so have a clear affinity during weathering and associated mobilisation and are, generally speaking, partitioned into the same minerals (e.g. plagioclase).

In contrast, Figure 3.18 shows that the most prominent enrichment trend is to be found in the lead content of the rock samples. There is no obvious single factor that might cause the lead concentration to be increased in the weathered fraction, but there could be several plausible hypotheses. One such explanation might be that the lead has concentrated itself in the weathered fraction due to leaching from the fresh rock fraction. However, this seems unlikely as lead is usually considered fluid mobile. If the lead had been leached to the surface layer, then it should surely also have been quickly lost during weathering. An alternative, and more plausible, explanation is the lead enrichment in the weathered samples might be due to the presence of lichen. Previous work examining lichen has suggested that they are a very effective sink for atmospheric heavy metals (Taylor *et al.*, 1998). Since some of the rock samples had abundant lichen growth, it is possible that the lead concentration may have been raised in the weathering rind despite the removal of surface lichen prior to analysis.

3.5.3. Weathering patterns derived from critical element ratios

After establishing which elements were conservative and which elements are non-conservative, the next aspect of the work involved an attempt to identify weathering patterns from the geochemical data. The purpose of this exercise was two-fold. The resulting weathering patterns will be used: i) in conjunction with actual streamwater chemistry data (Chapter 4) to underpin our understanding of the controls on headwater stream chemistry; and ii) in comparison with modelled weathering rates (Chapter 5) to assess the accuracy and usefulness of this methodology (i.e. using geochemical data from rocks for predictive purposes in the field of streamwater chemistry).

In hydrological systems, the base cation supply from weathering is of prime importance in determining the resulting streamwater chemistry. Therefore, given that calcium has shown the largest depletion from the weathered fraction (Section 3.5.1), it

would be logical to suggest that the "lost" calcium has entered the soil and stream environment. For this reason, it would be useful to assess whether the loss of calcium from the rocks is reflected in surface-water chemistry. The first step in this process is to examine the fresh and weathered composition of the individual rock samples. However, calcium is a major element, and as mentioned beforehand, is subject to the constant sum problem. Therefore, a trace element that exhibits similar behaviour to calcium is required to obviate the constant sum problem. As established in the previous section, strontium and calcium have a clear affinity during weathering and associated mobilisation and are, generally speaking, partitioned into the same minerals. Therefore, during this section strontium is used as a surrogate for calcium weathering.

Rather than comparing the direct strontium loss from the rock samples, a technique often employed in geochemistry is to plot an immobile element (e.g. zirconium) against the ratio of a mobile element (e.g. strontium) and the same immobile element (i.e. zirconium). This technique gives a good indication of the element mobility, since the change in ratio is solely the result of a change in the mobile element abundance rather than any spurious data anomalies. The individual data of the Borrowdale Volcanic Group is examined by plotting the weathered and fresh geochemical data on a Zr versus Sr/Zr diagram (Figure 3.19).

Figure 3.19 - Diagram showing the degree of weathering in the Borrowdale Volcanic Group using Sr/Zr ratio over Zr.

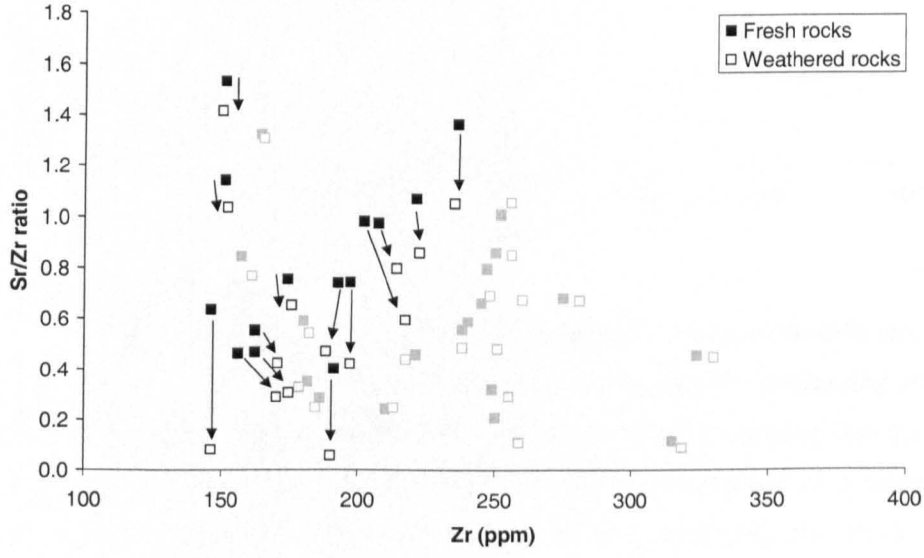


Figure 3.19 shows that approximately half (18) of the Borrowdale Volcanic Group rock samples show little or no difference in the Sr/Zr ratio between the fresh and weathered

fractions. In contrast, the other half (16) of the samples from Borrowdale Volcanic Group display a marked difference in the Sr/Zr ratio between the weathered and fresh fractions. The weathering differences between the individual rock samples may help to explain the heterogeneity in the water chemistry of streams draining the Borrowdale Volcanic Group (Section 4.3). At this stage, it would be fair to assume that the differing depletion of strontium (and presumably calcium) from the rock samples during weathering causes a differential base cation supply to streams. A comparison is made between the rock data and modelled catchment weathering rates produced by MAGIC later in the thesis (Section 5.4).

The individual data of the Skiddaw Slates and Silurian Slates groups were also examined by plotting the weathered and fresh geochemical data on a Zr versus Sr/Zr diagram (Figure 3.20).

Figure 3.20 - Diagram showing the degree of weathering in the Silurian Slates and Skiddaw Slates using Sr/Zr ratio over Zr.

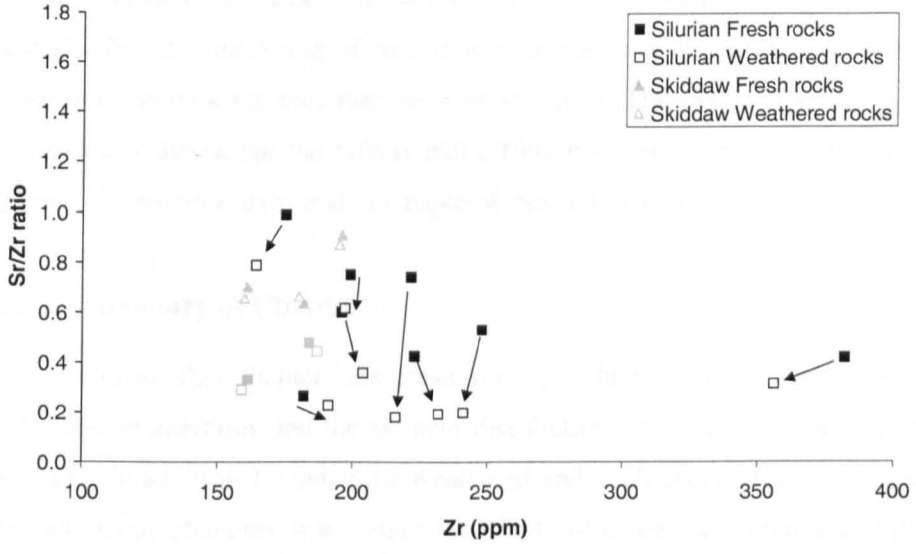


Figure 3.20 shows that the Skiddaw Slates show little or no difference in the Sr/Zr ratio between the fresh and weathered fractions. The lack of weathering in the Skiddaw Slates may help to explain the low alkalinity of the streams draining this geological group (Section 4.3). In contrast, the Silurian Slates, with the exception of 2 samples, display a significant difference in the Sr/Zr ratio between the weathered and fresh fractions. The degree of weathering in the Silurian Slates may help to explain the high base cation loadings and high alkalinities in the streams draining the Silurian Slates (Section 4.3). The rock data is compared with the modelled catchment weathering rates produced by MAGIC later in the thesis (Section 5.4).

Upon closer examination of Figure 3.19, it was discovered that the weathering patterns of the Borrowdale Volcanics rock samples are not apportioned into the separate rock types (i.e. andesites and dacites). On the contrary, there are 11 andesites and 7 dacites in the "low" weathering group compared to 10 andesites and 6 dacites in the "high" weathering group. In contrast, the samples in Figure 3.20 reflect the overall relationship with the individual rock type (i.e. greywackes and lithic arenites). The lithic arenite samples, in general, show the least depletion during weathering - the two non-weathering samples are lithic arenite. Whereas, the greywacke samples have a significantly larger depletion during weathering.

The weathering patterns of the Borrowdale Volcanics rock samples require another explanation for the differences in weathering which are not dependent on rock type. The most plausible explanation is that the different weathering patterns are due to variations in the weathering environment of the rocks. There are a multitude of variations which may be responsible for the diverse weathering patterns. Perhaps the most important of these are: i) varying lengths of rock's exposure to surface weathering processes; ii) altering susceptibility to weathering of rock due to orientation; and iii) different amounts of acid deposition the rock samples may have experienced. The first two variables lie beyond the scope of this thesis, but the effects that differing amounts of acid deposition can cause to bedrock chemistry is explored in Chapter 4 (Section 4.3.3).

3.6. Summary of Chapter

During this chapter, the fresh rock geochemical data was subjected to several classification exercises and the element distribution was examined by a series of variation diagrams. In addition, by using the weathered and fresh geochemical data, the behaviour of the individual elements was determined and subsequently formulated into some broad weathering patterns.

The 35 samples of the Borrowdale Volcanic Group were initially classified into seven rock types by the total alkalis-silica diagram. However, after a further classification (Winchester and Floyd, 1977) and some group abridging, the rock samples were assigned into two rock types (21 andesites and 14 dacites). The 12 samples of the Silurian Slates were classified into two rock types (7 greywackes and 5 lithic arenites) by the classification of Pettijohn *et al.* (1972). In addition, there were 3 metamorphosed Skiddaw Slates and a granite sample.

The major-element geochemistry variation diagrams suggested that the rock samples are very variable within, as well as between, the geological groups. The

Borrowdale Volcanic Group (~51 wt % to ~70 wt % silica) is very heterogeneous and displays the largest range in element compositions. The Silurian Slates has two distinct sub-groups - sub-group 1 (~57–62 wt % silica) has higher levels of all the metals, with the exception of sodium, than sub-group 2 (~66–70 wt % silica). The Skiddaw Slates (~51–57 wt % silica) is the most homogeneous geological group despite the transition metals tending to have larger data spreads than the other elements. The trace-element geochemistry variation diagrams also suggested that the Borrowdale Volcanic Group is the most heterogeneous group with the largest range in element concentrations. Sub-group 1 of the Silurian Slates has higher concentrations of the transitional metals than sub-group 2, whilst the concentrations of the HFS and LFS groups are very similar in both sub-groups. The Skiddaw Slates are the most homogeneous of the geological groups. The most plausible explanation for the heterogeneity of the Borrowdale Volcanic Group geochemical data seems to be that different amounts of fractionation are occurring within the rock samples. Whereas, the difference in the Silurian Slate sample compositions are most likely explained by the mineralogical maturity hypothesis (cf. Bhatia, 1983).

The geochemical data of the weathered and fresh fractions of the rock samples suggested that the majority of the elements exhibited fairly conservative behaviour. Of the 'unconservative' elements, calcium and strontium displayed the most prominent depletion pattern and lead demonstrates the most prominent enrichment pattern. Given that strontium exhibited a large depletion pattern, it was used to establish the weathering patterns of the geological groups. The strontium weathering patterns of the Borrowdale Volcanics were not linked to the separate rock types (i.e. andesites and dacites), but were most likely caused by variations in the weathering environment of the rocks. In contrast, the strontium weathering patterns of the Silurian Slates have some sort of relationship with the individual rock type (i.e. greywackes tend to be more susceptible to strontium depletion during weathering). The strontium weathering patterns of the Skiddaw Slate samples suggest that very little or no change has occurred to their composition during weathering.

In summary, the Borrowdale Volcanic Group exhibits the most heterogeneous element geochemistry, behaviour and weathering. The Silurian Slates (as one geological group) is also heterogeneous, but to a lesser extent than the Borrowdale Volcanics. However, the Silurian Slates seem fairly homogeneous if the two sub-groups are considered as separate geological groups. The Skiddaw Slates exhibit the most homogeneous geochemistry, behaviour and weathering.

CHAPTER 4

Major-ion chemistry of Lake District streams in relation to catchment characteristics

"Now the River is rich, collecting minerals & sticks.
Rain brought fatness, but she takes ninety-nine percent
Leaving the fields just one percent to survive on.
Now the river is poor. She is east wind sick
She huddles in holes and corners. The sun gives her a headache.
She has lost all her fish. And she shivers."
- 'The River in March' by Ted Hughes

4.1. Introduction

This chapter begins with a brief description of the way the catchment characteristics were calculated using Geographical Information System (GIS) software (Section 4.2). A fuller description of the GIS methodology and the raw catchment information can be found in Appendix F. During the course of this research, streamwater samples were collected from the study catchments and analysed using ion chromatography (Appendix B). The details of the raw geochemical data for the laboratory standards and the streamwater samples can be found in Appendix C and D respectively.

The stream chemistry data were analysed in four phases: (1) Major ion chemistry of streams draining the Lake District during the six surveys and the role of geology, land use and soil (Section 4.3.1); (2) Flow-weighted chemistry of the streams and the role of geology, land use, soil and atmospheric deposition (Section 4.3.2); (3) Using geochemical data as an aid for investigating the relative contributions of each geological group to streamwater chemistry (Section 4.3.3); and (4) Using space as a surrogate for time to assess the effects of land use conversion and/or climate change (Section 4.3.4).

The geochemical data from some of the sites in this study were compared with historical published data from these sites. This allowed the survey results to be put into context and allowed an assessment of whether any change in water chemistry had taken place during the intervening period.

4.2. Using GIS for comparing multiple datasets: Identification of catchment characteristics

Geographical Information Systems (GIS) are excellent tools for the automation, analysis, display and management of geographic information. Several previous studies have successfully used GIS to explore the relationships between catchment characteristics and stream water chemistry (Kalkhoff, 1993; Herlihy *et al.*, 1998; Kernan and Allott, 1998; Rigina, 1998). In addition, GIS has been used to explore the relationships between catchment characteristics and surface water critical loads (Hall *et al.*, 1995b; Kernan, 1995, 1996; Kernan *et al.*, 1998). The GIS package used for this study was ARC/INFO - a vector based GIS (E.S.R.I., 1989). GIS techniques allow the comparison of different datasets relating to the same area to be analysed. The GIS enabled information from maps and satellite imagery to be converted into digital spatial coverages.

A digital plot of the rivers draining the Lake District was created using the Institute of Hydrology Digital Terrain Model (IHDTM). A hard copy of the Lake District's rivers and contour lines was produced using a mapping package called DEGENER8 (Institute of Hydrology in-house computer program developed by Rob Flavin and Dave Morris). This computer-generated hard copy of the rivers was manually laid on top of a 1:50,000 geology map held in the library at British Geological Survey, Keyworth. Because this project focuses on the importance of geology to water chemistry (Criterion 1 - Section 2.2.7), most stream catchments were underlain by one or two (but occasionally up to three) geological units. Approximately 100 streams were chosen in this first selection; these were then located on 1:25,000 GRIDRANGER Ordnance Survey maps. After a reconnaissance trip in March 1996, the 100 sites were reduced to 55 sites due to considerations of accessibility and disturbance (Criteria 2 and 3 – Section 2.2.7). The actual grid references of the sites were finalised during the reconnaissance trip and these were used to generate the catchment areas for the study streams.

A computer program called GRIDLOOK (Institute of Hydrology in-house software developed by Oliver Swain) enables many kinds of gridded data to be viewed in a number of different text formats. In the context of this study, it was used for locating grid references of the stream sampling points to a resolution of 50 metres on the IHDTM. The grid references derived using GRIDLOOK were then entered into another computer program, TSTCD (Institute of Hydrology in-house software developed by Dave Morris), which generates catchment boundaries from a single grid reference using topography information (i.e. contours) from the IHDTM. In addition to generating the catchment boundary, TSTCD estimates catchment rainfall, runoff and potential evaporation using information from the

IHDTM.

The catchment boundaries created by TSTCD were entered into ARC/INFO. The catchments were labelled by grid reference and treated as individual polygons by ARC/INFO. The polygon information file, which contained each catchment boundary, was superimposed onto the soil, geology, land cover and deposition datasets. This exercise allowed each catchment to be characterised according to the percentage areal coverage of the different geology, land use, soil and atmospheric deposition loads. The percentage areal coverages within each catchment would be related to the catchment water chemistry thus forming the basis for the development of a simple empirical model (Chapter 5).

The following sub-sections discuss the source and limitations of the regional data used in the study (Section 4.2.1); the aggregation of this regional data (Section 4.2.2); and the classification into catchment characteristics (Section 4.2.3).

4.2.1. Sources and limitations of the regional data

a. Solid Geology

The original basis of the catchment selection was the predominant geology, derived from 1:50,000 geology maps. However, since the maps are held under licence by the British Geological Survey, direct copying and subsequent digitisation of the maps is prohibited. As the 1:50,000 geology map of the Lake District is not currently digitised, the British Geological Survey provided a licenced digital copy of the 1:250,000 Lake District geology map (B.G.S., 1980) for the purposes of this project.

The 1:250,000 solid geology map for the Lake District consists of 19 map units (Table 4.1) and provides an interpretation of the area's solid geology, but it does not show local surficial deposits (such as till and alluvium) resulting from recent Pleistocene glaciations. However, the spatial cover of these surficial deposits is relatively small within the study area. In addition, the physical (rather than chemical) classification of the map units means that they may not be lithologically and geochemically homogeneous. Despite the inconsistencies in the 1:250,000 map, it is the best regional indication of the Lake District's bedrock and is adequate for the purposes of this thesis.

Table 4.1 – Classification of individual map units of the 1:250,000 solid geology map of the Lake District (B.G.S. 1980).

Geological Map Unit	Era	Epoch	Rock Type
SEDIMENTARY FORMATIONS			
Coniston Limestone	Ordovician	Ashgill	Limestone Calcareous mudstone Calcareous siltstone
Stockdale Shales	Silurian	Llandovery	Graptolitic Mudstone Shale
Brathay Flags	Silurian	Wenlock	Graptolitic Siltstone
Coniston Grits	Silurian	Ludlow	Greywacke
Bannisdale Slates	Silurian	Ludlow	Mudstone Siltstone
Kirkby Moor Flags	Silurian	Ludlow	Greywacke
Mell Fell Conglomerate	Carboniferous	Dinantian	Conglomerate
Carboniferous Limestone	Carboniferous	Dinantian	Limestone
IGNEOUS ROCKS			
Basalt	Ordovician	Llandeilo	Basic Lava
Andesite	Ordovician	Llandeilo to Caradoc	Intermediate Lava
Rhyolite	Ordovician	Llandeilo to Caradoc	Acid Lava
Undifferentiated Tuffs	Ordovician	Llandeilo to Caradoc	Mostly intermediate tuffs
Intrusive rocks (Coarse grained)	Ordovician to Silurian	-	Granite Granophyre Granodiorite
METAMORPHIC ROCKS			
Skiddaw Slates	Ordovician	Arenig	Metamorphosed Mudstone Metamorphosed Siltstone

Table 4.2 – Classification of individual map units of the Soil Survey map of the Lake District (Jarvis *et al*, 1984a,b) showing the proportion of each HOST class (Boorman *et al*, 1995) attributed to each soil unit.

Soil Map Unit	HOST Class	Percentage of Soil Unit
Skiddaw	15	33.33
	27	53.33
	29	13.33
Bangor	27	57.14
	29	42.86
Powys	17	33.33
	22	66.67
Denbigh 1	4	13.33
	17	60.00
	18	13.33
	22	13.33
Denbigh 2	6	18.60
	8	17.44
	9	17.44
	17	46.51
Manod	17	87.50
	22	12.50
Malvern	4	28.57
	19	71.43
Hexworthy	15	100.00
Hafren	15	86.67
	26	13.33
Cegin	17	11.76
	18	11.76
	24	76.47
Wilcocks 1	10	11.11
	26	88.89
Wilcocks 2	15	11.11
	26	55.56
	29	33.33
Winter Hill	29	100.00

b. Soils

The Hydrology of Soil Types (HOST) classification (Boorman *et al.*, 1995) was used as the soil variable in this study. The classification was derived from Soil Survey maps (Avery, 1980) and eleven conceptual models describing the dominant processes of water movement through the soil and substrate. These models fall into three physical settings: (i) The soil overlies a permeable substrate with water table depth greater than 2m; (ii) The soil overlies a permeable substrate with a water table within 2m; and (iii) No significant groundwater aquifer but a shallow impermeable substrate impedes vertical movement of water. By subdividing the soils into 3 physical settings, the HOST classification is an ideal way of estimating the role of hydrological parameters within a wide range of catchments.

The HOST data set is obtained by applying the classification to the 1km National soil maps (i.e. Avery, 1980). Firstly, the soil units in each 1km from Soil Survey's 1:250,000 soil maps are identified, then the appropriate HOST classifications are applied to all map units. The proportion of each HOST class in each survey catchment is thus calculated. The HOST map for the Lake District consists of 13 Soil map units and 15 HOST class units (Table 4.2).

A digital version of the HOST classification (provided by the Institute of Hydrology) was used for the purposes of this study. HOST classifications for small catchments were also validated by hand.

c. Land Use

The Land Cover Map of Great Britain (Fuller *et al.*, 1994a) was used for the Land Use data in the project. The map uses high-resolution satellite imagery data from the Landsat Thematic Mapper. The classification's accuracy was substantially improved by using a combination of summer and winter data (Fuller *et al.*, 1994b). The Land Cover map records 25 cover types (Table 4.3) and is based on 25m grid squares. It is available at 2 resolutions, (i) Actual land cover in a 25m x 25m grid square; and (ii) Dominant land cover in a 1km x 1km grid square. A digital version of the Land Cover map showing the dominant land cover at $1km^2$ resolution (provided by the Institute of Terrestrial Ecology) was used for the purposes of this study as it is the best regional indication of land use.

Since the land cover data only indicates the dominant land cover class in $1km^2$ it may not accurately represent land cover diversity below $1km^2$ resolution. However, this resolution should prove adequate for the purposes of the thesis with the size of the study catchments ranging between 0.3 and 11.7 km^2.

Table 4.3 – Classification of individual map units from the Land Cover map of Great Britain (Fuller *et al*, 1994a,b).

Land Use Unit	Land Cover Class
1	Sea / Estuary
2	Inland Water
3	Beach & Coastal bare
4	Saltmarsh
5	Lowland Grass Heath
6	Pasture / Grazed Turf
7	Meadow / Semi-natural veg
8	Rough / Marsh Grass
9	Moorland Grass / Hill Grass
10	Grass Moorland / Dwarf Shrub
11	Upland Dwarf Shrub Moorland
12	Bracken
13	Dense Shrub Heath
14	Shrub / Orchard
15	Deciduous Wood
16	Coniferous Wood
17	Upland Bog
18	Arable Land / Tilled Land
19	Ruderal Weed
20	Suburban / Rural development
21	Urban
22	Inland Bare Ground
23	Felled Forest
24	Lowland Bog
25	Open Shrub Heath

d. Atmospheric deposition

Thirty-two UK monitoring stations measure the amount of wet deposition for selected ions (hydrogen, sulphate, nitrate, ammonium, sodium, chloride, magnesium, calcium, potassium and phosphate) on a daily to weekly basis. In addition, there are 38 UK monitoring stations measuring the concentrations of atmospheric gases (used as a surrogate for cloud and dry deposition) on a daily to weekly basis. These sites were set up by Warren Springs Laboratory (Stevenage, UK) and are currently managed by AEA Technology (Abingdon, UK). By using the geostatistical technique of kriging (which provides the best interpolated estimate), the precipitation-weighted annual mean fluxes of these ions and

gases was calculated and mapped for 20km x 20km grid squares covering the whole UK.

As part of the UK critical loads work (CLAG, 1995; Hall *et al.*, 1995b), the deposition data was recalculated into the following components using the sum of the kriged wet plus dry plus cloud deposition (All values are keq ha^{-1} yr^{-1}):

- Total base cation (Ca^{2+} + Mg^{2+}) deposition (TOTBC)
- Non-Marine base cation (Ca^{2+} + Mg^{2+}) deposition (NMBC)
- Total sulphur deposition (TOTS)
- Non-marine sulphur deposition (NMS)
- Oxidised nitrogen deposition (NOx)
- Reduced inorganic nitrogen deposition (NHx)

The mean annual fluxes of these components for the period 1989-92 (displayed as several 20km x 20km digital grids provided by the Institute of Terrestrial Ecology) was used for the purposes of this study. The 20km x 20km digital data grids show the spatial distribution of each component's annual flux and thus provide the best available regional dataset of atmospheric deposition in the Lake District. However, actual atmospheric deposition may vary by large amounts (up to 50% - c.f. UKRGAR, 1997) over a 20km by 20km grid square due to variations in factors such as altitude differences (Choularton *et al.*, 1988; Fowler *et al.*, 1988; Dore *et al.*, 1992), land use (Hornung and Adamson, 1991; Neal *et al.*, 1992b,c; Stevens *et al.*, 1994; Nisbet *et al.*, 1995) and proximity to the sea (Sutcliffe and Carrick, 1983b; Hultberg *et al.*, 1994). The problem of the 20km x 20km data was also recognised by Critical Loads Advisory Group on Freshwaters (Kreiser *et al.*, 1993; CLAG, 1995; Hall *et al.*, 1995a) who suggested that data at this resolution should be used extremely cautiously when attempting to identify deposition at the catchment scale.

4.2.2. Aggregation of the regional data

a. Geology

The 1:250,000 solid geology map of the Lake District consists of 19 units, of which 13 lie within the study catchments (Table 4.4). The 13 units were further aggregated according to the existing British Geological Survey classification of (i) Borrowdale Volcanics - including undifferentiated tuffs, andesite, rhyolite and basaltic lavas, (ii) Silurian Slates - incorporating five geological units (Coniston grits, Bannisdale Slates, Kirkby Moor Flags, Stockdale Shales and Brathay Flags) with several shale, siltstone, mudstone and greywacke facies, (iii) Skiddaw Slates - consisting of metamorphosed mudstones and siltstones, (iv) Intrusive rocks – in this case granite; and (v) Carbonate rocks

- mostly limestone and calcareous siltstone (cf. Chapter 3).

Table 4.4 – Aggregation of individual map units from the 1:250,000 solid geology map of the Lake District (B.G.S., 1980) into five categories, also showing the buffering capacity class (Edmunds and Kinniburgh, 1986).

Aggregated Category	Map Units	Buffering Class
Borrowdale Volcanic Group	Andesite Lava	2
	Rhyolite Lava	1
	Undifferentiated Tuffs	2
	Basaltic Lava	2
Skiddaw Slates Group	Metamorphosed Mudstone	2
	Metamorphosed Siltstone	2
Intrusive Rocks	Granite	1
Silurian Slates Group	Greywacke	2
	Mudstone (including graptolitic)	2
	Siltstone (including graptolitic)	2
	Shale	2
Carbonates	Limestone	4
	Calcareous Siltstone	3

The underlying geology is very important in catchment buffering and a summary of the chemical processes underlying neutralisation of rainfall acidity takes place below.

[1] Reaction of bicarbonate in water

$$H_2O + CO_2 \longleftrightarrow 2H^+ + CO_3^{2-}$$

[2] Dissolution of carbonate minerals in soils and rocks

$$2H^+ + CaCO_3 \longrightarrow H_2O + CO_2 + Ca^{2+}$$

Calcium leached from the system due to strong acid anions

[3] Hydrolysis of silicate minerals in soils and rocks (using feldspar)

$$2H^+ + 2KalSi_3O_8 + 9H_2O \longrightarrow 2Kal_2(OH)_4Si_2O_5 + 4Si(OH)_4$$

(Acid) (Feldspar) (water) (kaolinite) (silicate)

Base cations leached with bicarbonate or strong acid anions

[4] Cation exchange with soils

$$2H^+ + Ca^{2+}\,(soil) \longrightarrow 2H^+\,(soil) + Ca^{2+}$$

Calcium is leached with strong acid anions

The physical classification (i.e. rock types divided into sedimentary, metamorphic and igneous classes) used by British Geological Survey may have little bearing on the surface water chemistry. Therefore, on the basis of the knowledge gleaned in Chapter 3, the mineralogy and expected weathering products of the major bedrock types were assigned (Table 4.5). In addition, the geological units were also aggregated into four 'buffering capacity' groups (Table 4.4. - c.f. method of Edmunds and Kinniburgh, 1986).

Table 4.5 – Mineralogy and expected weathering products for the major bedrock types in the Lake District

Bedrock Type	Major mineralogy Minor mineralogy	Weathering products
Borrowdale Volcanics	Quartz	SiO_2
	K-Feldspar	K, SiO_2, HCO_3
	Plagioclase	Ca, Na, SiO_2, HCO_3
	Augite	Ca, SiO_2, HCO_3
	Chlorite	Mg, SiO_2, HCO_3
	Calcite	Ca, HCO_3
	Amphibole	Ca, Mg, SiO_2, HCO_3
	Magnetite	FeO
	Muscovite	K, SiO_2, HCO_3
Granite	Quartz	SiO_2
	K-Feldspar	K, SiO_2, HCO_3
	Plagioclase	Ca, Na, SiO_2, HCO_3
	Biotite	Mg, K, SiO_2, HCO_3
	Chlorite	Mg, SiO_2, HCO_3
	Epidote	Ca, SiO_2, HCO_3
	Magnetite	FeO
Silurian Slates	Quartz	SiO_2
	K-Feldspar	K, SiO_2, HCO_3
	Pyrite	FeO
	Haematite	FeO
	Calcite	Ca, HCO_3
Skiddaw Slates	Quartz	SiO_2
	K-Feldspar	K, SiO_2, HCO_3
	Sericite	K, SiO_2, HCO_3
	Muscovite	K, SiO_2, HCO_3
	Magnetite	FeO
Carb Limestone	Calcite	Ca, HCO_3

b. Land Use

Of the 25 classes on the Land Cover map, 10 lie within the study catchments. Based on biogeochemical knowledge and a 'ground truthing' exercise, the land cover data was aggregated into three land use categories (i) Upland Vegetation - incorporating five land cover types; (ii) Agriculture - incorporating three land cover types; and (iii) Forested - incorporating two land cover types (Table 4.6).

Table 4.6 – Aggregation of individual map units from the Land Cover Map of Great Britain (Fuller *et al*, 1994a,b) into three categories.

Aggregated Category	Map Units
Upland Vegetation	Moorland Grass / Hill Grass (Class 9) Grass Moorland / Dwarf Shrub (Class 10) Upland dense Shrub Moor (Class 11) Bracken (Class 12) Upland Bog (Class 17)
Agriculture	Lowland Grass Heath (Class 5) Pasture / Grazed Turf (Class 6) Meadow / Semi-natural veg (Class 7)
Forestry	Deciduous Woodland (Class 15) Coniferous Woodland (Class 16)

c. Soils

Of the 29 units on the HOST map of the Lake District, 15 lie within the study catchments. Using a subdivision of the HOST classification, based on permeability and soil depth, the soil data was aggregated into four categories (i) Thick and porous soil - incorporating four HOST soil units; (ii) Thin and impermeable soil - incorporating four HOST soil units; (iii) Gleyed soil - incorporating three HOST soil units; and (iv) Peaty soil – incorporating four HOST soil units (Table 4.7). Since the method for aggregating the soil data was already a sub-division of the HOST classification, no alternative was deemed necessary for assessing the validity of the grouping.

Table 4.7 – Aggregation of individual map units from the HOST map of the Lake District (Boorman *et al*, 1995) into four categories.

Aggregated Category	Map Units
Thick & Porous Soil	Host Class 4 Host Class 5 Host Class 8 Host Class 17
Thin & Impermeable soil	Host Class 18 Host Class 19 Host Class 21 Host Class 22
Gleyed Soil	Host Class 9 Host Class 10 Host Class 24
Peaty Soil	Host Class 15 Host Class 24 Host Class 26 Host Class 27

d. Atmospheric Deposition

The atmospheric deposition map for the Lake District consisted of nine 20km by 20km deposition grids. These data were reduced to seven 'deposition loading' regions because three of the grids possessed similar values to each other. The grids were labelled 'DEP1' through 'DEP7' on the basis of increasing loads of base cations and acid anions (Table 4.8). Since this method of calculating atmospheric deposition should be used with extreme caution at the catchment scale, an alternate method of calculating deposition was also used during this aspect of the project to assess the accuracy of the kriged data.

Table 4.8 – Seven deposition load categories abridged from the estimated average annual deposition values derived for the UK Critical Loads work
(Values in keq ha^{-1} yr^{-1}).

Loading	TOTBC	NMBC	NOx	NHx	TOTS	NMS
DEP 1	0.7	0.2	0.4	0.7	1.0	0.8
DEP 2	0.9	0.3	0.4	0.7	1.4	1.1
DEP 3	1.1	0.4	0.5	1.0	1.7	1.4
DEP 4	1.3	0.3	0.5	0.9	1.8	1.3
DEP 5	1.4	0.4	0.6	1.0	2.1	1.6
DEP 6	1.7	0.5	0.8	1.7	2.5	1.9
DEP 7	2.3	0.6	1.0	1.8	3.1	2.3

The Cl balance method utilises rainfall data, which is recalculated based on the assumption that chloride is conservative, which is a common way of calculating catchment specific rainfall chemistry (Jenkins *et al.*, 1997). The rainfall data comes from the raingauge at Bannisdale (NY 515043) which has been sampled weekly since 1986. The chloride input flux was enhanced / reduced according to the following formula:

$$Cl_{dep} * AP = Cl_{str} * AR$$

where Cl_{dep} is the total deposition concentration of chloride (wet, dry and occult);
AP is the annual volume of precipitation in metres;
Cl_{str} is the measured concentration in streamwater; and
AR is the annual runoff in metres.

The enhancement / reduction of chloride input is assumed to be sea-salt driven. Therefore, base cations and sulphate are also added / removed in the appropriate sea-salt ratio to maintain the pH of the rainfall. The deposition concentrations were recalculated using the following formula:

$$BC_{dep} = BC_{wet} + (f_{ss} * Cl_{er})$$

where BC_{dep} is total deposition of base cations (wet, dry and occult);
BC_{wet} is the observed wet deposition concentration;
f_{ss} is the sea-salt fraction (where Na^+=0.86, Ca^{2+}=0.04, Mg^{2+}=0.21, K^+=0.019 and SO_4^{2-}=0.104);
Cl_{er} is the change in chloride calculated from the input-output mass balance.

The resulting deposition concentrations from the Cl balance method were recalculated again into fluxes (keq ha^{-1} yr^{-1}) using the following formula:

$$DEP_{flux} = (DEP_{conc} * Ppte_{amt}) * 100$$

where DEP_{flux} is the calculated annual deposition flux of the chosen ion (in keq ha^{-1} yr^{-1});
DEP_{conc} is the deposition concentration (annual mean) of the chosen ion; and
$Ppte_{amt}$ is the annual volume of precipitation at the given site.

The 'Cl balance method' atmospheric deposition fluxes were also aggregated into seven 'deposition loadings' which were labelled 'CLDEP1' through 'CLDEP7' on the basis of increasing loads of sulphate and nitrate (Table 4.9).

Table 4.9 – Estimated average annual deposition ranges calculated using the Cl balance deposition method. (Values in keq ha^{-1} yr^{-1}).

Loading	Nitrate	Non-Marine Sulphate
CLDEP 1	0.5 to 0.6	1 to 1.2
CLDEP 2	0.61 to 0.7	1.21 to 1.4
CLDEP 3	0.71 to 0.8	1.41 to 1.6
CLDEP 4	0.81 to 0.9	1.61 to 1.8
CLDEP 5	0.91 to 1.0	1.81 to 2.0
CLDEP 6	1.01 to 1.1	2.01 to 2.2
CLDEP 7	Above 1.1	Above 2.2

The advantage of this approach is that it is more likely to reflect individual catchment characteristics (e.g. altitude differences and sea-salt influences) than the 20 by 20km grid deposition estimates. The disadvantages of this approach are the assumption that chloride is conservative (i.e. no catchment chloride source) and the inherent errors in using ion-balance methodology. Previous work (Sutcliffe and Carrick, 1983b) has suggested that the chloride concentrations of some streams in the Lake District are not conservative which might suggest a catchment source of chloride (e.g. from the bedrock or anthropogenic sources like road salting). In addition, errors in the initial deposition chemical data can be magnified during recalculation (Rowntree, 1981; Cohen, 1988) so great care should also be taken when interpreting the ion-balance deposition data.

4.2.3. The classification of catchment characteristics using GIS

The raw catchment information (i.e. full GIS details) and the aggregated catchment characteristics for each of the 55 study catchments can be found elsewhere (Appendix F). The areal coverage of the aggregated regional data was determined by the GIS methodology for each catchment and was subsequently used for statistical analysis (Chapter 5). However, Edmunds and Kinniburgh's 'geological sensitivity' method was not used during the rest of this thesis since the areal coverage of the 13 geological units was predominantly apportioned to buffering category 2 (See Table 4.6), therefore, not enough data spread was evident for statistical or descriptive data analysis.

For the purposes of the stream survey aspect of the thesis (Section 4.3), the

catchments were classified using the criteria in Table 4.10. The aggregated groups are as before, except the mixed lithology category has replaced the 'carbonate rock' category.

Table 4.10 – Criteria used for the classification of the 55 study catchments.

Catchment Characteristic	Classification criteria for catchments	N
Borrowdale Volcanic Group	Catchments with > 65 % Borrowdale Volcanics	n=30
Skiddaw Slates Group	Catchments with > 65 % Skidaw Slates	n=3
Granite	Catchments with > 25% Granite	n=3
Silurian Slates Group	Catchments with > 65 % Silurian Slates	n=11
Mixed Lithology	Catchments with any amount of carbonate bedrock; **or** Catchments with no dominant bedrock.	n=8
Upland Vegetation	Catchments with > 80% Upland Vegetation	n=41
Forested	Catchments with > 80% Forested land	n=3
Agriculture	Catchments with > 25% Agriculture	n=11
Thick / Porous soil	Catchments with > 25% THP soil	n=14
Thin / Impermeable soil	Catchments with > 25 % THI soil	n=12
Gleyed Soil	Catchments with > 25% GLY soil	n=2
Peaty Soil	Catchments with > 75% PTY soil; **or** Catchments where the other soils have < 25% and PTY soil is dominant.	n=27
DEP 1	Catchments with 100% DEP 1	n=2
DEP 2	Catchments with 100% DEP 2	n=3
DEP 3	Catchments with 100% DEP 3	n=7
DEP 4	Catchments with 100% DEP 4	n=3
DEP 5	Catchments with 100% DEP 5	n=10
DEP 6	Catchments with 100% DEP 6	n=16
DEP 7	Catchments with 100% DEP 7	n=14

4.3. Stream survey results

The 55 Lake District streams chosen using the selection criteria (Section 2.2.7) were sampled over the period May 1996 – March 1997, in six synoptic surveys. Streamwater samples were collected every two months and incorporated a variety of flow conditions. These stream chemistry data was analysed in four phases: (1) Individual survey major-ion chemistry; (2) Flow-weighted chemistry; (3) Catchment contributions to water chemistry;

and (4) Future water chemistry estimates.

4.3.1. Major-ion chemistry from the six individual surveys and an assessment of the role of geology, land use and soil

A version of this section has been published in the paper: GJP Thornton & NB Dise (1997). Major-ion chemistry of the streams draining the English Lake District (Cumbria), *Proceedings of the Sixth Annual Symposium of the British Hydrological Society, Salford University, 15-19th September 1997, p2.17-2.24.*

During the first phase of the stream chemistry work, the concentrations in the 55 streams of major ions, alkalinity and silica, as well as the discharge were examined for each trip individually. Prior to the analyses, the hydrological regime of the study period was compared with historical flow conditions to put the survey results in context (Section 4.3.1a). The chemical data was compared with the catchment characteristics of geology, land use and soil in three phases: (i) Examining the inter-relationships within the data using a correlation matrix (Section 4.3.1b); (ii) Examining the seasonal patterns in the chemical data using graphs categorised by geology, land use and soils respectively (Section 4.3.1c); and (iii) Examining the baseflow and stormflow of the streams independent of catchment characteristics (Section 4.3.1d).

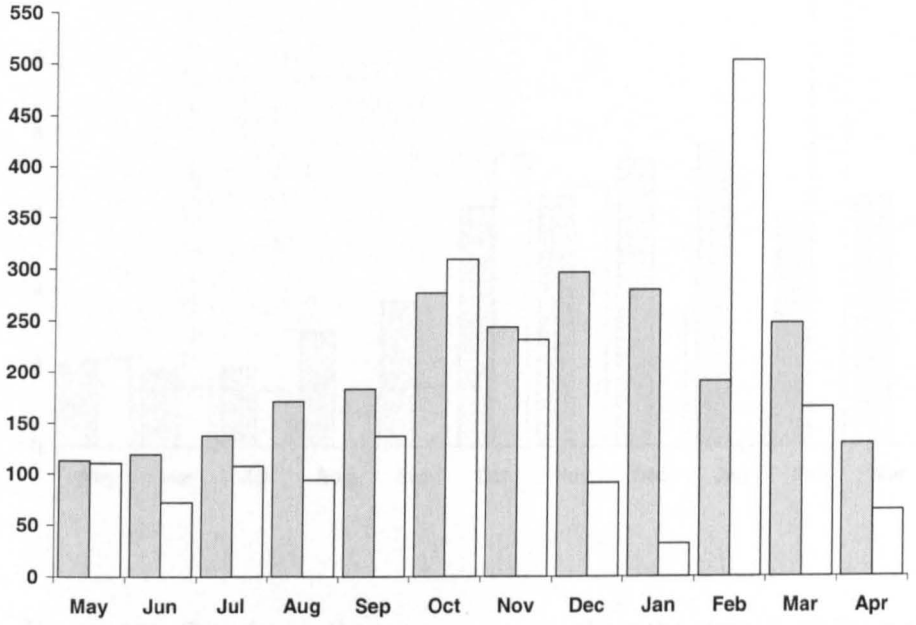
a. Hydrological regime of the study period related to historical flow conditions

The hydrological regime of the study period was related to historical flow conditions using data provided by the National Water Archive at the Institute of Hydrology. The data was available in a number of formats, but only monthly catchment rainfall, daily streamflow and monthly streamflow for the period 1981 to 1997 were used for the purpose of this study. The National Water Archive collates data from approximately 100 gauging and meteorological stations in the North-West region, of which eight stations were chosen based on their proximity to the study area and the completeness of their historical records. These stations are: River Duddon at Ulpha (SD 209947), River Duddon at Duddon Hall (SD 196896), River Sprint at Sprint Mill (SD 514961), River Kent at Burneside (SD 507956), River Derwent at Portinscale (NY 251239), Haweswater beck at Burnbanks (NY 508159), River Eamont at Pooley Bridge (NY 472249) and River Mint at Mint Bridge (SD 524944).

To ascertain whether the study year fitted in with the norm, or whether it was unusually wet or dry, the mean monthly value of the catchment rainfall from the eight

stations was calculated for the period, 1981-95, and was compared with similar data for the survey year. (Figure 4.1).

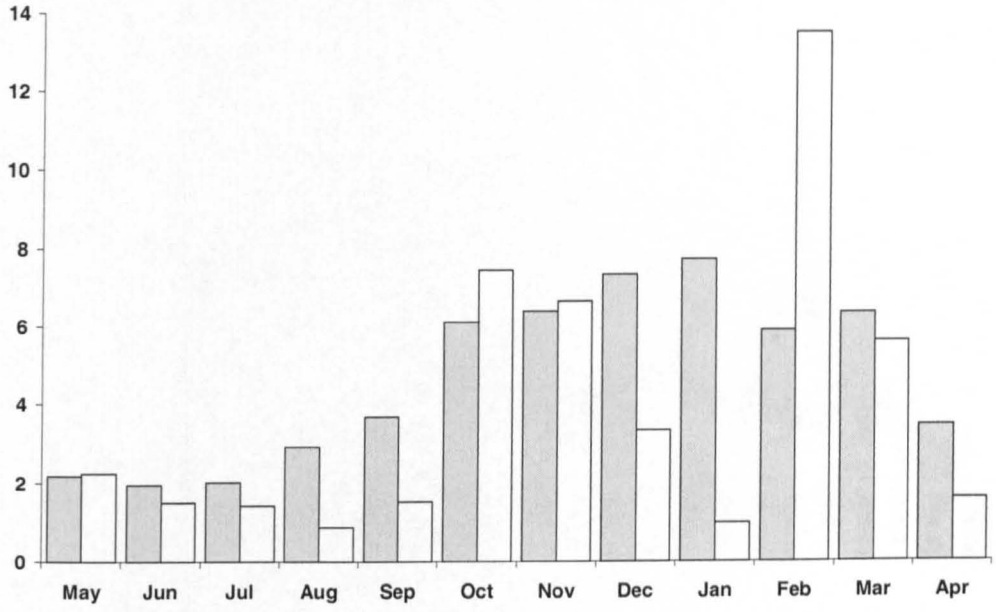
Figure 4.1 - Mean monthly catchment rainfall measured at 8 meteorological stations, 1981-95 (stippled bars) compared with mean monthly catchment rainfall for the survey period, 1996-97 (open bars). (Units are millimetres)



The annual rainfall in the survey year (1917 mm) was notably less than the annual value of the long-term average (2388 mm). The monthly distribution of the rainfall was also different. The monthly rainfall data in the survey year was about the same (± 10 %) as the 1981-95 average in May, October and November, but it was significantly less than the average for eight months of the year (June, July, August, September, December, January, March and April). The survey year seemed to have a slightly drier summer and a much drier winter than the long-term average. The rainfall in February (505 mm) was over twice the amount of the long-term average (191 mm) but this unusually wet month did not result in the survey year being a wetter than average year.

The mean monthly flow from the eight stations was also calculated for the period 1981-95, and was compared with similar data for the survey year. (Figure 4.2).

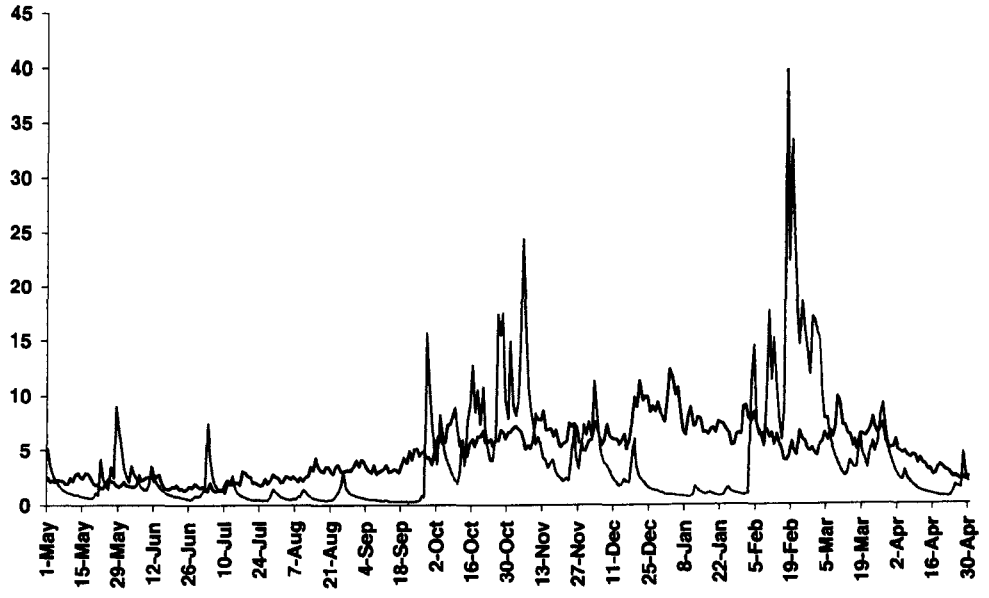
Figure 4.2 - Mean monthly flow from 8 gauged sites, 1981-95 (stippled bars) compared with mean monthly flow for the survey period, 1996-97 (open bars). (Units are $m^3 sec^{-1}$).



The monthly flow data in the survey year was about the same (± 10 %) as the 1981-95 average in May, November and March, but it was significantly less than the average for seven months of the year (June, July, August, September, December, January and April). For the remaining two months, October and February, the monthly flow data was notably higher than the long-term average. On the whole, the survey year had lower flows in summer and winter than previously recorded (i.e. long-term average). Unsurprisingly, the monthly flow data replicates the patterns identified in the catchment rainfall data. For example, the flow in February (13.5 $m^3 sec^{-1}$) was over twice the amount of the long-term average (5.9 $m^3 sec^{-1}$), which corresponds with the high rainfall identified in Figure 4.2.

Using monthly data is extremely useful for identifying the broad trends in the rainfall and flow data. However, the drawback of this data is that an overall smoothing of the data often occurs, which may result in some important individual events being overlooked. For this reason, the daily flow data from the eight stations was calculated for the study period and compared with similar data for the period 1981-95, to allow the extreme events to be identified (Figure 4.3).

Figure 4.3 - Average daily flow data from 8 gauged stations, 1981-95 (blue line) compared with average daily flow data for the survey period, 1996-97 (red line). (Units are $m^3 sec^{-1}$)



The daily flow data was significantly less than the average for two sustained periods during the survey year. The first period, 17 July – 25 September, was a period of extremely low flow (mostly below 0.5 $m^3 sec^{-1}$) and there were no peaks above the long-term average (usually around 3 $m^3 sec^{-1}$). The second period, 4 December – 5 February, was also a period of extremely low flow (mostly below 1 $m^3 sec^{-1}$) and no peaks were above the long-term average (usually between 5 – 10 $m^3 sec^{-1}$). These periods of extremely low flow are visible in the monthly data patterns (Figure 4.2), which also suggest that July, August, September, December and January were significantly below the long-term average.

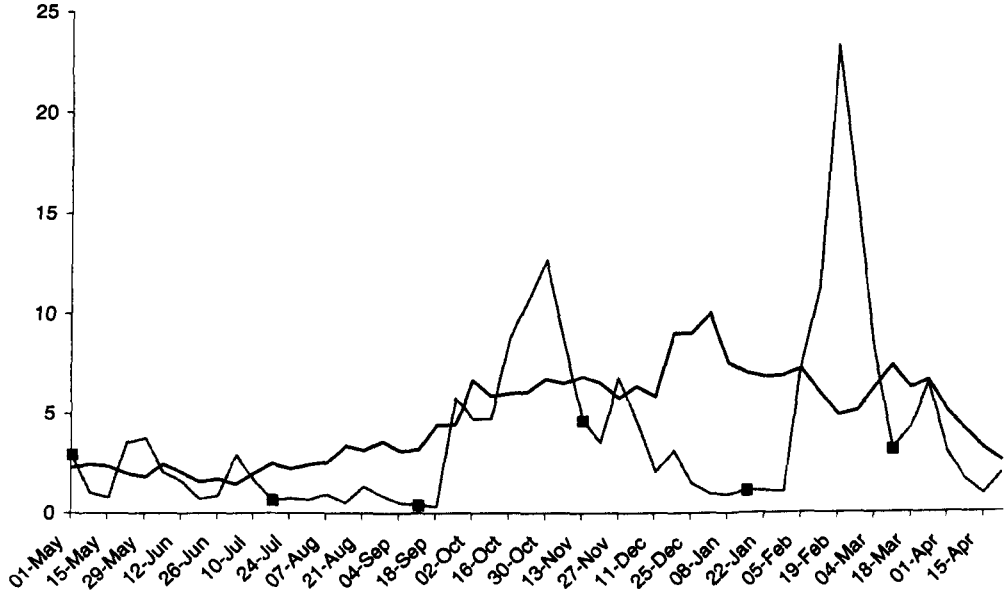
The daily flow data was significantly higher than the average for three periods during the survey year. The first period, 1 May – 29 May, has four peaks (between 4 – 9 $m^3 sec^{-1}$) that are significantly above average (circa 3 $m^3 sec^{-1}$), but there is also a period of low flow (less than one cumec) between 8 – 22 May. Therefore, the monthly flow data suggests that May's flow is very similar for the survey year compared with the long-term average (Figure 4.2). The second period, 25 September – 4 December, has nine peaks (between 10 – 25 $m^3 sec^{-1}$) that are significantly above average (between 5 – 8 $m^3 sec^{-1}$), and three 'troughs' which are below average (between 2 – 3 $m^3 sec^{-1}$). The monthly flow data suggests that the flow in October is higher than average, whilst the flow in November is very similar to the long-term average (Figure 4.2). The third period, 5 February – 5 March, has seven peaks (between 15 – 40 $m^3 sec^{-1}$) that are significantly above average (between 4

– 9 m^3 sec^{-1}). The extremely unusual high-flow events identified from the daily data in February are replicated by monthly data (Figure 4.2).

On the whole, the majority of the high-flow and low-flow events have been recognised in the monthly data patterns. However, the monthly data considers May to be very similar to the long-term average, but May has four high-flow events which might prove very important for biota survival. High-flow events are often associated with 'acid episodes' (Davies *et al.*, 1992), and a stream's response to these episodes in spring is critical to its ability to sustain healthy biota populations (Whitehead *et al.*, 1988a).

During this study, water samples were collected on a bimonthly basis. The infrequent nature of this sampling means it is entirely possible that the six synoptic surveys did not encompass the whole range of flow conditions. Therefore, the survey week could have fallen during (or missed) the highest / lowest flow period and the resulting streamwater chemistry might be unduly biased. The daily flow data were recalculated into weekly flow data for the study year as well as the long-term average. By examining the weekly flow data, it is possible to assess whether the six sampling weeks are in context with the 'mean' flow by comparing them with the both the survey year and the long-term average (Figure 4.4).

Figure 4.4 - Mean weekly flow from 8 gauged sites for 1981-95 (blue line) and 1996-97 (red line) compared with flow data during each synoptic survey week (black squares). (Units are m^3 sec^{-1})



The survey weeks are lower than average flow but reflect the flow during the year as a whole (Figure 4.4). Both 'November' and 'March' sample weeks were at the end of high flow periods, and therefore reflect 'flushed-through' (i.e. stormflow like) conditions, whereas other sampling weeks are indicative of baseflow conditions.

Overall, if the two periods of extremely high flow are excluded, the six sampling weeks seem to be fairly representative of the survey year. However, the unintentional bias caused by the sampling regime missing these two periods of peak flow may have implications for the streamwater chemistry results. Concentrations of base cations and alkalinity are usually highest in low flow conditions and lowest in high flow conditions. Therefore, were stream sampling to have occurred during the high-flow periods then the base cation and alkalinity concentrations would be significantly lower, and hence the streams could be perceived as more 'sensitive'. It is, therefore, logical to suggest that the bias inflicted by this sampling regime is likely to result in an underestimation, which is more preferable to an overestimation, of the impact of acid precipitation on the study area. However, the use of ion concentrations in streams has several inherent problems, which are fully discussed in Section 4.3.2.

b. Correlations between the major-ion chemistry and catchment characteristics

The chemical data from the six synoptic surveys and the catchment characteristics were examined using a correlation matrix (Table 4.11). The correlation matrix was used as a preliminary assessment of the study data, as well as to identify any notable relationships and interactions within the data. At this point of the research, I was not examining the cause and effect between variables and recognise that some of the correlations in this section are spurious due to two apparently correlated factors being correlated to a third factor. An in depth assessment of the interactions between the variables can be found in Chapter 5, where a full statistical treatment of the study data occurs. The correlation coefficients that are statistically significant at the 1% level are shaded.

Table 4.11 – A correlation matrix showing correlations between ion concentrations in the stream and catchment characteristics for the 55 study catchments.
(Data from all six surveys (N=330). Shaded values ($r > 0.232$) are statistically significant at the 1% level ($p < 0.01$)).

	pH	Na	Mg	Ca	K	Cl	NO_3	SO_4^{2-}	Alk	SiO_2	BVG	SKS	SIL	MIX	GR	UPL	FOR	AGR	D1	D2	D3	D4	D5	D6	D7	THP	THI	GLY
Na	0.05																											
Mg	0.52	0.58																										
Ca	0.62	0.57	0.79																									
K	0.52	0.34	0.69	0.72																								
Cl	0.08	0.81	0.44	0.56	0.49																							
NO_3	0.19	0.43	0.32	0.63	0.56	0.56																						
SO_4^{2-}	0.28	0.61	0.54	0.58	0.50	0.66	0.44																					
Alk	0.61	0.47	0.85	0.85	0.56	0.23	0.30	0.29																				
SiO_2	0.20	-0.07	0.19	0.21	0.25	-0.01	0.05	-0.12	0.26																			
BVG	-0.06	-0.35	-0.29	-0.39	-0.32	-0.38	-0.37	-0.38	-0.25	-0.21																		
SKS	-0.26	0.05	0.01	-0.11	-0.04	0.08	-0.12	0.12	-0.11	-0.06	-0.34																	
SIL	0.23	0.30	0.26	0.51	0.36	0.35	0.50	0.33	0.33	0.28	-0.83	-0.16																
MIX	0.10	0.03	0.21	0.06	0.10	-0.10	-0.08	0.04	0.19	-0.03	-0.25	-0.07	0.12															
GR	-0.14	0.17	-0.01	-0.17	-0.05	0.18	-0.07	0.01	-0.15	-0.08	-0.01	-0.08	-0.17	-0.07														
UPL	-0.25	-0.31	-0.27	-0.55	-0.38	-0.34	-0.56	-0.28	-0.38	-0.41	0.68	0.12	-0.86	0.09	0.17													
FOR	0.02	0.17	-0.04	0.12	0.03	0.24	0.06	0.27	-0.02	0.19	-0.35	-0.07	0.45	-0.07	-0.08	-0.57												
AGR	0.29	0.25	0.36	0.58	0.44	0.24	0.64	0.14	0.48	0.37	-0.57	-0.10	0.71	-0.06	-0.15	-0.80	-0.05											
D1	-0.14	0.03	0.06	-0.03	0.03	-0.06	-0.06	-0.09	0.08	0.05	-0.17	0.57	-0.12	-0.05	-0.06	0.01	-0.06	0.02										
D2	-0.02	0.02	0.00	-0.08	-0.03	0.06	-0.11	0.04	-0.08	0.18	0.02	0.28	-0.14	-0.06	-0.07	0.14	-0.06	-0.13	-0.05									
D3	0.21	0.31	0.34	0.54	0.41	0.32	0.63	0.17	0.42	0.25	-0.55	-0.10	0.68	-0.02	-0.11	-0.65	-0.11	0.87	-0.07	-0.09								
D4	-0.17	0.15	-0.02	-0.18	-0.05	0.16	-0.08	0.02	-0.17	-0.08	-0.13	0.28	-0.14	-0.06	0.59	0.14	-0.07	-0.13	-0.05	-0.06	-0.09							
D5	-0.03	0.04	-0.11	-0.07	-0.05	0.09	-0.02	0.08	-0.14	0.01	-0.17	-0.12	0.26	-0.11	0.06	-0.30	0.57	-0.05	-0.09	-0.11	-0.17	-0.11						
D6	0.22	-0.26	0.10	0.02	-0.02	-0.36	-0.22	-0.10	0.18	0.06	0.22	-0.18	-0.18	0.33	-0.09	0.27	-0.19	-0.19	-0.13	-0.16	-0.26	-0.16	-0.30					
D7	-0.21	-0.09	-0.28	-0.23	-0.21	-0.02	-0.10	-0.09	-0.29	-0.33	0.46	-0.16	-0.35	-0.15	-0.12	0.31	-0.11	-0.30	-0.11	-0.14	-0.22	-0.14	-0.26	-0.39				
THP	0.10	0.33	0.30	0.48	0.40	0.37	0.59	0.33	0.28	0.17	-0.77	0.33	0.66	0.10	-0.13	-0.62	0.08	0.70	0.06	0.03	0.69	0.00	-0.05	-0.22	-0.29			
THI	0.16	-0.01	0.02	0.16	0.06	-0.02	0.20	-0.05	0.12	0.07	0.16	-0.22	-0.04	-0.11	0.04	-0.07	-0.19	0.23	-0.18	-0.25	0.21	-0.07	-0.26	0.06	0.24	0.30		
GLY	0.13	0.05	0.20	0.15	0.10	0.04	-0.02	0.08	0.19	0.16	-0.25	0.03	0.27	-0.01	-0.06	-0.12	-0.09	0.20	0.24	-0.03	0.14	-0.09	-0.14	0.11	-0.14	0.10	-0.05	
PTY	-0.18	-0.25	-0.29	-0.46	-0.35	-0.27	-0.51	-0.24	-0.32	-0.20	0.58	-0.16	-0.55	-0.02	0.10	0.52	0.05	-0.67	-0.05	0.09	-0.63	0.06	0.18	0.10	0.17	-0.88	-0.59	-0.39

The majority of the chemical determinands have significant positive correlations with the other chemical determinands (ranging from 0.25 between silica and potassium to 0.85 between alkalinity and calcium / magnesium). Significant correlations were not found between pH and sodium (0.05), chloride (0.08) and nitrate (0.19), and between silica and pH (0.20), sodium (-0.07), magnesium (0.19), calcium (0.21), chloride (-0.01), nitrate (0.05) and sulphate (-0.12). In general, the base cations (calcium, magnesium and potassium) are strongly related with each other as well as with alkalinity. In addition, sodium and chloride are also strongly related due to their natural chemical affinity in sea-salt, which is to be expected with a maritime region like the Lake District.

The majority of the chemical data was negatively correlated with Borrowdale Volcanic geology (%), ranging from -0.39 for calcium to -0.25 for alkalinity. A significant correlation was not found for pH (-0.06). All the chemical data was positively correlated with the Silurian Slate geology (%), ranging from 0.51 for calcium to 0.23 for pH. Significant correlations were not found between the chemical data and the Skiddaw Slates (%), Granite (%) and Mixed Lithology (%) geology categories. In general, the relationships between the chemical data and the Borrowdale Volcanics (%) are moderate, whereas calcium and nitrate concentrations are strongly related to the Silurian Slates (%).

All the chemical data was negatively correlated to upland vegetation (%), ranging from -0.56 for nitrate to -0.25 for pH. The majority of the chemical data was positively correlated to agriculture (%), ranging from 0.64 for nitrate to 0.24 for sodium. A significant correlation was not found for sulphate (0.14). Chloride (0.24) and sulphate (0.27) were positively correlated to forested land (%). On the whole, the relationships between the chemical data and land use are moderate, with the exception of calcium and nitrate concentrations, which are strongly related to upland vegetation and agriculture.

The majority of the chemical data was positively correlated with % deposition load 3 (DEP 3), ranging from 0.63 for nitrate to 0.25 for silica. Significant correlations were not found for pH (0.21) and sulphate (0.17). Sodium (-0.26) and chloride (-0.36) were negatively correlated with % deposition load 6 (DEP 6), whilst magnesium (-0.28), alkalinity (-0.29) and silica (-0.33) were negatively correlated with % deposition load 7 (DEP 7). Significant correlations were not found between the chemical data and the other four deposition loads (DEP 1, 2, 4 and 5). Overall, the relationships between the chemical data and % deposition loads are weak. The strongest relationships with the chemical data, particularly calcium and nitrate concentrations, were with % deposition load 3 (DEP 3). However, the association between DEP 3 and elevated base cations, alkalinity and nitrate is likely spurious as the majority of the agriculture-dominated catchments receive this

deposition load (a fact identified by the strong positive relationship found in Table 4.11).

The majority of the chemical data was positively correlated with % thick, porous soil (THP), ranging from 0.59 for nitrate to 0.28 for alkalinity. Significant correlations were not found for pH (0.10) and silica (0.17). The majority of the chemical data was negatively correlated to % peaty soil (PTY), ranging from -0.51 for nitrate to -0.24 for sulphate. Significant correlations were not found for pH (-0.18) and silica (-0.20). Significant correlations were not found between the chemical data and % thin, impermeable soil (THI) and % gleyed soil (GLY). Generally, calcium and nitrate concentrations exhibited the strongest relationships with THP soil and PTY soil.

Summary

There were some strong correlations between the chemical data, most noticeably calcium and nitrate concentrations, and the catchment characteristics (Table 4.11). The chemical data was negatively correlated with percentage Borrowdale Volcanic geology, upland vegetation, DEP 7 and PTY soil. However, these four catchment characteristics exhibit strong positive correlations with each other. This might suggest that they would be found together in stream catchments. In contrast, the chemical data was positively correlated with percentage Silurian Slates, agriculture, DEP 3 and THP soil. Furthermore, they also seem to exhibit strong positive correlations with each other, which also suggests that they might be found together in stream catchments.

c. *Examining concentration differences and seasonal patterns in major-ion chemistry related to catchment characteristics* [#]

The variations in the major ion chemistry, alkalinity, silica and stream discharge during the individual surveys were examined in relation to the geology, land use and soil of the sites. The streams were examined in this way to establish seasonal changes in major-ion chemistry, as well as to establish the behaviour differences of the individual groups.

GEOLOGY

The chemical data from the individual surveys were categorised according to rock type (Figure 4.5). Prior to data analysis, the Silurian Slates were divided into two sub-groups based on presence / absence of agriculture. The decision to divide this group was made

[#] **NOTE:** The monthly chemical data are not examined in relation to atmospheric deposition because it was only available as annual mean flux. In addition, data for potassium (K^+) are not examined because concentrations of this ion are nearly always very low (90% of monthly concentrations are below 5 $\mu eq\ l^{-1}$), and data for phosphate (PO_4^-) and ammonium (NH_4^+) are not examined because the concentrations of these two ions are always below the detection limit.

because a high proportion of the agriculture areal coverage exists on this geological group. This decision was supported by the strong positive correlation found between Silurian Slates and agriculture on the correlation matrix (Table 4.11).

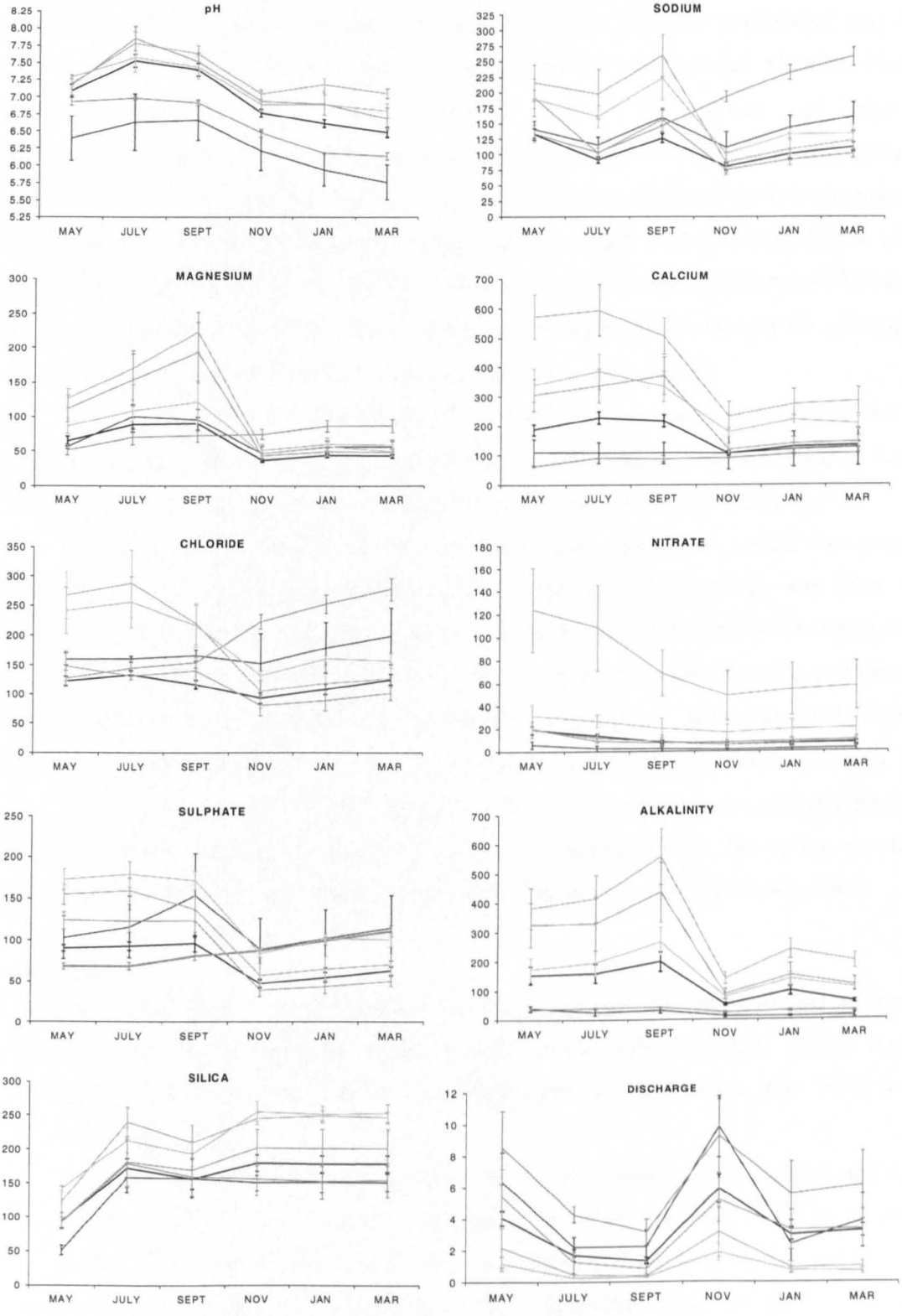
Categorising the chemical data by rock type suggests that some ions exhibit large differences between the geological groups and the individual surveys, whilst others show fairly low variability across the geological groups and surveys (Figure 4.5). For example, the calcium, nitrate and alkalinity concentrations show a high degree of variability across the geology types, which supports the findings of Chapter 3. In contrast, magnesium and silica concentrations exhibit moderate differences between the geology groups, while pH, sodium, chloride and sulphate concentrations (and discharge) seem to exhibit far less distinct differences between the geology groups.

High variability – Calcium concentrations are high in the Silurian Slates with agriculture catchments (up to 600 $\mu eq\ l^{-1}$), moderately high in the Silurian Slates with no agriculture and Mixed lithology catchments (up to 400 $\mu eq\ l^{-1}$), low in Borrowdale Volcanic catchments (150-200 $\mu eq\ l^{-1}$), and very low in Skiddaw Slate and Granite catchments (< 100 $\mu eq\ l^{-1}$). Nitrate concentrations are high in the Silurian Slates with agriculture catchments (up to 120 $\mu eq\ l^{-1}$), moderate in the Silurian Slates with no agriculture (up to 30 $\mu eq\ l^{-1}$), and low in the Borrowdale Volcanic, Skiddaw Slate, Granite and Mixed lithology catchments (< 20 $\mu eq\ l^{-1}$). Alkalinity is high in the Silurian Slates with agriculture catchments (up to 550 $\mu eq\ l^{-1}$), moderately high in the Silurian Slates with no agriculture catchments (up to 400 $\mu eq\ l^{-1}$), low in Borrowdale Volcanic and Mixed lithology catchments (up to 200 $\mu eq\ l^{-1}$), and very low in Skiddaw Slate and Granite catchments (< 50 $\mu eq\ l^{-1}$).

Moderate variability – Magnesium concentrations are high in the Silurian Slates with agriculture catchments (up to 250 $\mu eq\ l^{-1}$), moderately high in the Mixed lithology catchments (up to 200 $\mu eq\ l^{-1}$) and low in the Silurian Slates with no agriculture, Borrowdale Volcanic, Skiddaw Slate and Granite catchments (50-100 $\mu eq\ l^{-1}$). Silica concentrations are fairly high in the Silurian Slates with agriculture and the Silurian Slates with no agriculture catchments (up to 250 $\mu g\ l^{-1}$), moderate in the Borrowdale Volcanic and Mixed lithology catchments (up to 200 $\mu g\ l^{-1}$) and reasonably low in the Skiddaw Slate and Granite catchments (up to 150 $\mu g\ l^{-1}$).

Low variability – pH levels are fairly high in the Silurian Slates with agriculture, Mixed lithology, Borrowdale Volcanic and Silurian Slates with no agriculture catchments (pH 6.5-7.8), moderate in the Granite catchments (pH 6.2-7.0) and fairly low in the Skiddaw Slate catchments (pH 5.8- 6.5). Sodium concentrations are high in Silurian Slates

Figure 4.5 - Mean major ion concentrations and discharge of streams categorised by rock type. (Units are μeq l^{-1}, except silica (μg l^{-1}), discharge (m^3 sec^{-1}) and pH. Error bars are ± 1 S.E.).
Key: Black – Borrowdale Volcanics (n=30); Blue – Skiddaw Slates (n=3); Red – Granite (n=3); Pink – Mixed lithology (n=8); Green – Silurian Slates with agriculture (n=7); Turquoise – Silurian Slates no agriculture (n=4).



with agriculture, Granite and Silurian Slates with no agriculture catchments (200-250 μeq l^{-1}) and moderately high in the Borrowdale Volcanic, Mixed lithology and Skiddaw Slates catchments (100-200 μeq l^{-1}). Chloride concentrations are high in the Silurian Slates with agriculture, Granite and Silurian Slates with no agriculture catchments (200-300 μeq l^{-1}) and moderately high in the Borrowdale Volcanic, Mixed lithology and Skiddaw Slates catchments (100-200 μeq l^{-1}). The similarity between the sodium and chloride concentrations and seasonal patterns are probably due to the sea-salt ratio in atmospheric deposition, which might suggest that the streamwater concentrations of these two elements are mirroring precipitation. Sulphate concentrations are high in the Silurian Slates with agriculture, Skiddaw Slates and Silurian Slates with no agriculture catchments (150-200 μeq l^{-1}), moderately high in the Mixed lithology catchments (up to 120 μeq l^{-1}) and fairly low in the Granite and Borrowdale Volcanic catchments (< 100 μeq l^{-1}).

Discharge is high in the Skiddaw Slates and Granite catchments (up to 10 m^3 sec^{-1}), moderately high in the Borrowdale Volcanic and Mixed lithology catchments (up to 7 m^3 sec^{-1}) and fairly low in catchments of both Silurian Slate categories (up to 3 m^3 sec^{-1}).

In general, the Silurian Slates with agriculture catchments record the lowest discharge and the highest concentrations of the major ions, pH, alkalinity and silica. In contrast, either the Skiddaw Slates or Granite catchments record the highest discharge and the lowest concentrations in the study period. The majority of stream sites (the exceptions being Silurian Slates with agriculture, Silurian Slates with no agriculture and Mixed lithology catchments) record calcium concentrations and alkalinites below 200 μeq l^{-1} throughout the year. This is the threshold for sensitivity to acidification via acid deposition, which may have implications for biota survival / reproduction in the spring months (Altschuller and McBean, 1979; Hendrey *et al.*, 1980; Haines *et al.*, 1983; Linthurst, 1983).

LAND USE

The chemical data from the individual surveys was categorised according to land use type (Figure 4.6). By categorising the chemical data in this way some ions exhibit large differences between the groups and the individual surveys, whilst others show fairly low variability (Figure 4.6).

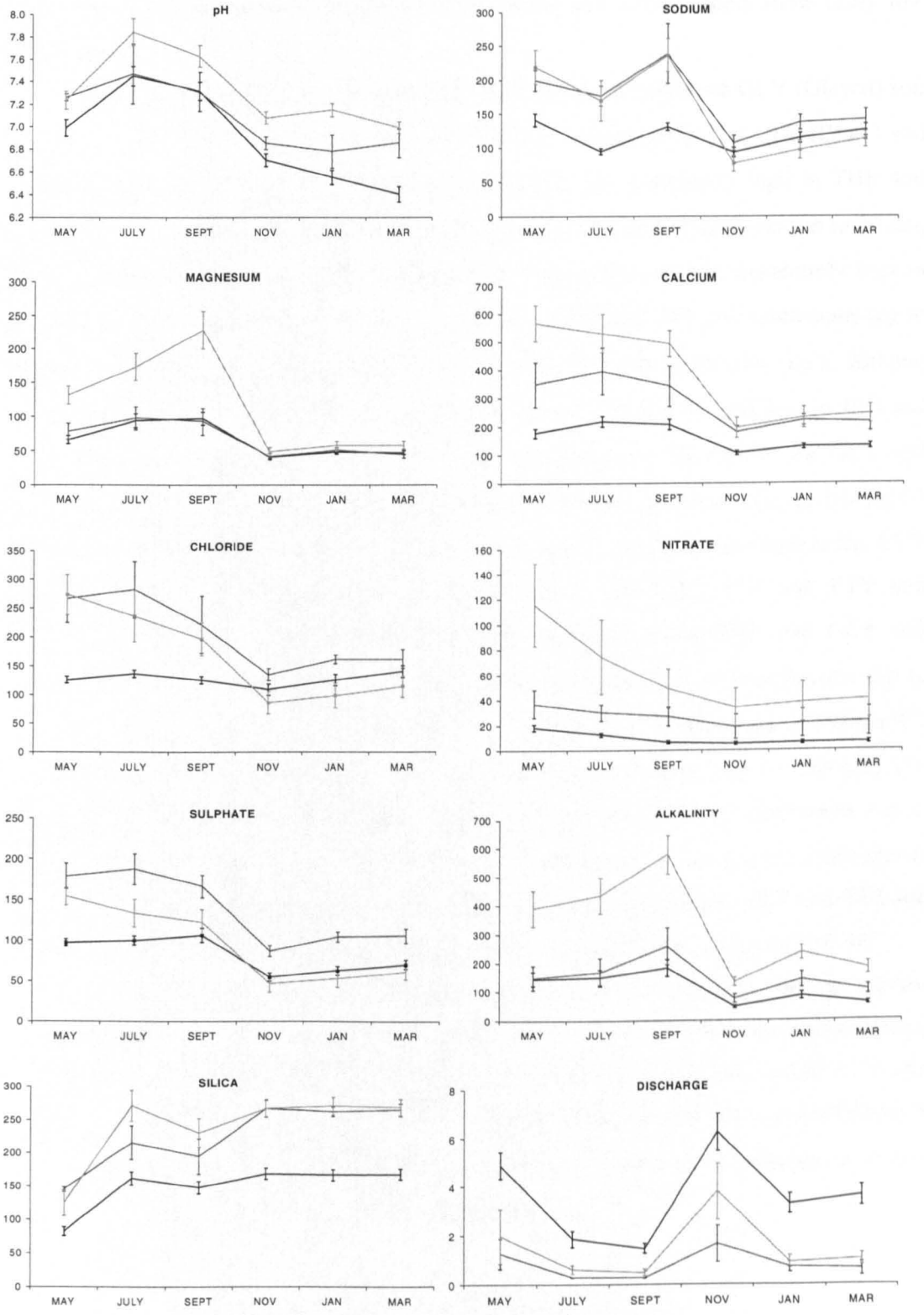
The strong correlations found between the Silurian Slates and agriculture, and the Silurian Slates and forestry (Table 4.11) suggested that these variables might be closely inter-related. This fact was borne out by an in-depth examination of the catchment characteristic data (Appendix F). The majority of agricultural land use resides on the Silurian Slates, and is thus almost identical to the Silurian Slates with agriculture group

used in Figure 4.6. In addition, all the forested land also resides on the Silurian Slates and is almost identical to the Silurian Slates with no agriculture group. Therefore, to avoid needless repetition, a detailed discussion of the behaviour of these groups is not required here – a full description /discussion is only made for upland vegetation from Figure 4.2.

The upland vegetation catchments have particularly low calcium concentrations (up to 200 $\mu eq\ l^{-1}$), compared with agricultural (up to 600 $\mu eq\ l^{-1}$) and forested (up to 400 $\mu eq\ l^{-1}$) catchments. Nitrate concentrations are very low in the upland vegetation catchments (< 20 $\mu eq\ l^{-1}$), compared with agricultural (up to 120 $\mu eq\ l^{-1}$) and forested (up to 40 $\mu eq\ l^{-1}$) catchments. Alkalinity in the upland vegetation catchments is very similar to the forested catchments (up to 200 $\mu eq\ l^{-1}$), but is much lower than in the agricultural catchments (up to 600 $\mu eq\ l^{-1}$). Magnesium concentrations in the upland vegetation catchments are very similar to the forested catchments (up to 100 $\mu eq\ l^{-1}$), but are significantly lower than in the agricultural catchments (up to 250 $\mu eq\ l^{-1}$). Silica concentrations are notably lower in the upland vegetation catchments (50-150 $\mu g\ l^{-1}$) than in the agricultural and forested catchments (150-250 $\mu g\ l^{-1}$). pH in the upland vegetation catchments is fairly similar to the forested catchments (pH 6.4-7.4), but is significantly lower than in the agricultural catchments (pH 7.2-7.8). Sodium concentrations in the upland vegetation catchments (100-150 $\mu eq\ l^{-1}$) are substantially lower than in the agricultural and forested catchments (up to 250 $\mu eq\ l^{-1}$). Chloride concentrations in the upland vegetation catchments (100-150 $\mu eq\ l^{-1}$) are considerably lower than in the agricultural and forested catchments (up to 300 $\mu eq\ l^{-1}$). Sulphate concentrations in the upland vegetation catchments (50-100 $\mu eq\ l^{-1}$) are lower than in the agricultural (50-150 $\mu eq\ l^{-1}$) and forested (100-200 $\mu eq\ l^{-1}$) catchments. Discharge in the upland vegetation catchments (up to 6 $m^3\ sec^{-1}$) is significantly higher than in the agricultural (up to 3 $m^3\ sec^{-1}$) and forested (up to 1.5 $m^3\ sec^{-1}$).

In general, the agriculture catchments record the highest concentrations of the major ions, pH, alkalinity and silica, the forested catchments record the lowest discharge and the highest sulphate concentrations, and the upland catchments record the highest discharge and the lowest ion concentrations. Calcium concentrations and alkalinities are commonly below 200 $\mu eq\ l^{-1}$ throughout the year at the majority of stream sites, except those in agriculture and forested catchments.

Figure 4.6 - Mean major ion concentrations and discharge of streams categorised by land use. (Units are μeq l^{-1}, except silica (μg l^{-1}), discharge (m^3 sec^{-1}) and pH. Error bars are ± 1 S.E.).
Key: Black – Upland Vegetation (n=41); Blue – Forested (n=3); Red – Agriculture (n=11).



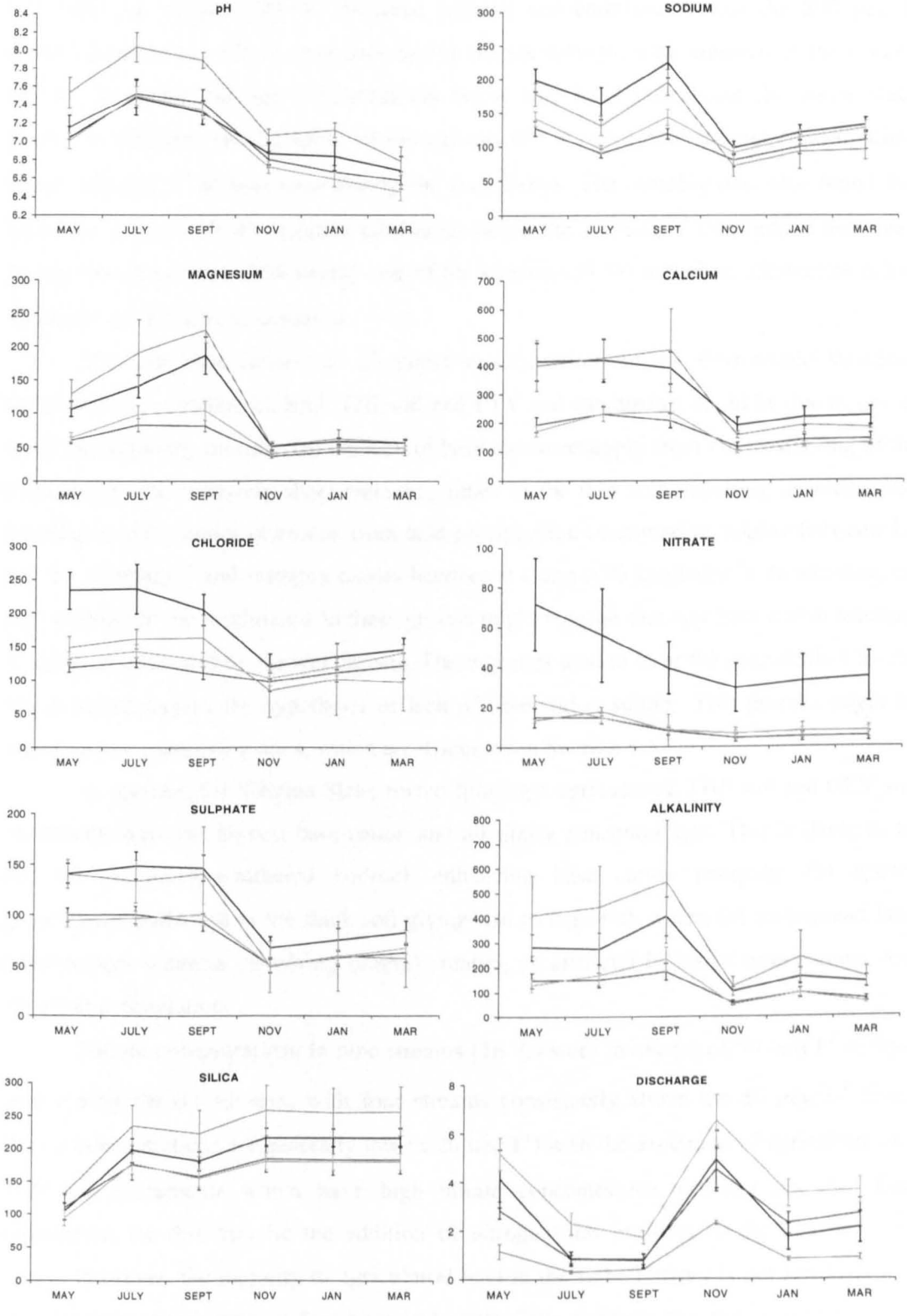
SOILS

The chemical data from the individual surveys was categorised according to soil type (Figure 4.7). By categorising the chemical data in this way some ions exhibit large differences between the groups and the individual surveys, whilst others show fairly low variability.

Calcium concentrations are high in the THP (Thick, porous) and GLY (Gleyed) soil catchments (up to 450 $\mu eq\ l^{-1}$) and low in THI (Thin, impermeable) and PTY (Peaty) soil catchments (up to 200 $\mu eq\ l^{-1}$). Nitrate concentrations are moderately high in THP soil catchments (up to 80 $\mu eq\ l^{-1}$) and low in THI, GLY and PTY soil catchments (up to 20 $\mu eq\ l^{-1}$). Alkalinity is high in the GLY soil catchments (up to 500 $\mu eq\ l^{-1}$), moderately high in the THP soil catchments (up to 350 $\mu eq\ l^{-1}$) and low in THI and PTY soil catchments (up to 200 $\mu eq\ l^{-1}$). Magnesium concentrations are high in the GLY soil catchments (up to 200 $\mu eq\ l^{-1}$), moderately high in the THP soil catchments (up to 150 $\mu eq\ l^{-1}$) and low in THI and PTY soil catchments (up to 100 $\mu eq\ l^{-1}$). Silica concentrations are high in the GLY soil catchments (up to 250 $\mu g\ l^{-1}$), moderately high in the THP soil catchments (up to 200 $\mu g\ l^{-1}$) and low in THI and PTY soil catchments (up to 150 $\mu g\ l^{-1}$). pH levels are high in the GLY soil catchments (pH 6.8-8.0) and moderately high in the THP, THI and PTY soil catchments (pH 6.4-7.4). Sodium concentrations are high in the THP and GLY soil catchments (up to 230 $\mu eq\ l^{-1}$), and moderate in the THI and PTY soil catchments (up to 150 $\mu eq\ l^{-1}$). Chloride concentrations are high in the THP soil catchments (up to 250 $\mu eq\ l^{-1}$) and moderately high in the THI, GLY and PTY soil catchments (up to 150 $\mu eq\ l^{-1}$). Sulphate concentrations are moderately high in the THP and GLY soil catchments (up to 150 $\mu eq\ l^{-1}$) and fairly low in the THI and PTY soil catchments (< 100 $\mu eq\ l^{-1}$). Discharge is high in PTY soil catchments (up to 6 $m^3\ sec^{-1}$), moderately high in the THP and THI soil catchments (up to 4 $m^3\ sec^{-1}$) and fairly low in the GLY soil catchments (up to 2 $m^3\ sec^{-1}$).

In general, the GLY soil catchments record the lowest discharge and the highest concentrations of the base cations, pH, alkalinity and silica, the THP soil catchments record the highest sodium and acid anion concentrations, and either the THI or the PTY soil catchments record the lowest ion concentrations. Calcium concentrations and alkalinity's are commonly below 200 $\mu eq\ l^{-1}$ threshold throughout the year at the majority of stream sites, except those in THP and GLY soil catchments.

Figure 4.7 - Mean major ion concentrations and discharge of streams categorised by soil type. (Units are μeq l^{-1}, except silica (μg l^{-1}), discharge (m^3 sec^{-1}) and pH. Error bars are ± 1 S.E.).
Key: Black – THP Soil (n=14); Blue – THI Soil (n=12); Red – GLY Soil (n=2); Green – PTY Soil (n=27).



SUMMARY

The mean monthly data of the six synoptic surveys were examined for major ions, pH, alkalinity, silica and discharge in relation to geology, land use and soil by Figures 4.5 to 4.7. Fifty-one streams (93 %) recorded calcium concentrations below the 200 μeq l^{-1} threshold (Section 1.1.2) at least once during the six surveys, with nineteen of the streams (35 %) recording calcium concentrations below this level throughout the entire study period. In addition, twenty-seven of the streams (49 %) recorded calcium concentrations below 100 μeq l^{-1} at least once during the six surveys. The monthly data also found that fifty-four streams (98 %) recorded alkalinities below the 200 μeq l^{-1} threshold at least once during the six surveys, with twenty-one of the streams (38 %) recording alkalinities below 50 μeq l^{-1} on at least one occasion.

The low base cation and alkalinity concentrations in the Borrowdale Volcanic, Skiddaw Slate, Granite, Upland, THI soil and PTY soil catchments could be due to any or all of the following reasons: (a) the lack of base cation resupply from the weathering of the bedrock; (b) the relatively short residence times in the thin soils resulting in widespread leaching; and (c) inputs of anions from acid precipitation (non-marine sulphur between 1.4 and 2.3 keq/ha/yr^{-1} and nitrogen oxides between 0.4 and 0.96 keq/ha/yr^{-1}). In addition, the high altitude of the catchments in these groups might suggest that any base cation leaching would be accentuated by the wet climate. These groups tend to have the lowest silica levels, which might support the hypothesis of lack of base cation supply. This process might be linked to low weathering rates, which are discussed in Section 4.3.3.

In contrast, the Silurian Slate, mixed lithology, agricultural, THP soil and GLY soil catchments have the highest base cation and alkalinity concentrations. This is likely to be due to: (a) easily-weathered bedrock enhancing base cation resupply, (b) deeper groundwater pathways in the thick soil giving rise to base-rich water, (c) widespread land improvement schemes (involving liming) creating an artificial influx of base cations, and (d) lower precipitation.

Nitrate concentrations in nine streams (16 %) were in excess of 50 μeq l^{-1} at least once during the six surveys, with four streams consistently above the 50 μeq l^{-1} level. Nitrate concentrations are generally low (< 20 μeq l^{-1}) with the exception of agriculture and THP soil catchments which have high nitrate concentrations (80-120 μeq l^{-1}). One explanation for this may be the addition of nitrogen-rich fertilizer to the land in early spring. However, the majority of agricultural land in the Lake District is not fertilized and only provides rough grazing for sheep and cattle. This suggests that the enhanced nitrate concentrations could possibly be attributed to animal waste. Research at the Institute of

Grassland and Animal Production found when nitrogen is returned in faeces and urine via grazed systems, the leaching loss of nitrate is up to six times higher than in a harvested and fertilized regime (Ryden *et al.*, 1984).

The sulphate concentrations are highest in Silurian Slate, agricultural, forested, GLY soil and THP soil catchments (150-200 $\mu eq\ l^{-1}$). In the Granite group, the sulphate peak in March may be due to increased atmospheric deposition, a fact that is supported by the elevated concentrations of sodium and chloride (which seem to be mirroring the sea-salt ratio in atmospheric deposition) during this time. The peak in the forested catchments could be due to preferential scavenging of atmospheric sea-spray by the trees (Neal *et al.*, 1992b). The large error bars in the Skiddaw Slates group might suggest there is significant intra-group variability in sulphate concentrations.

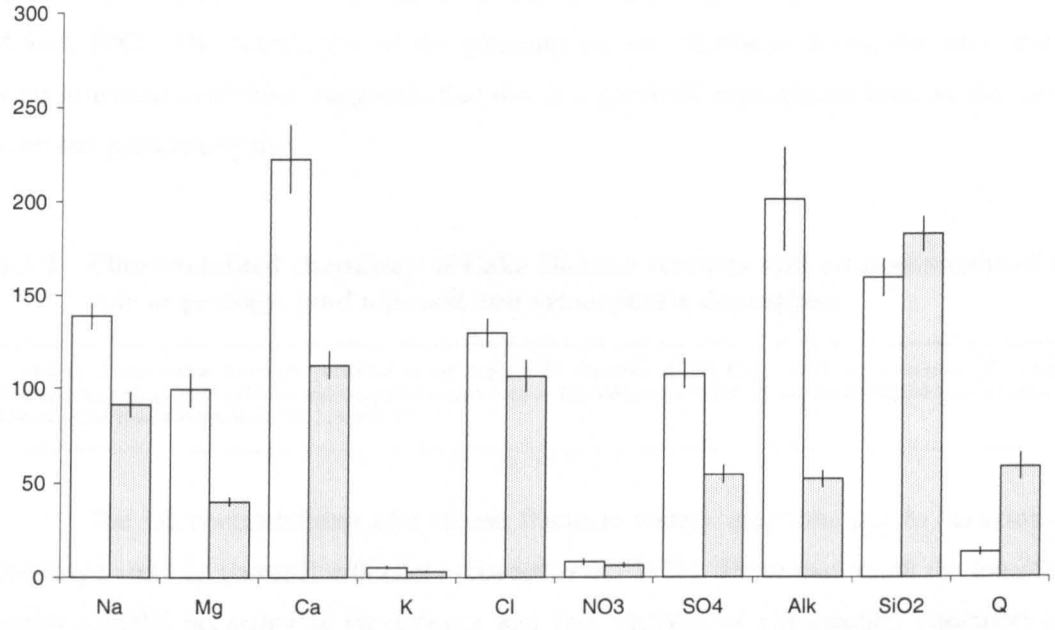
The monthly data seem to show that most 'peaks' occur in November, while most 'troughs' occur in September. These differences are explored by examining the streamwater chemistry under baseflow and stormflow conditions (Section 4.3.1d).

d. Baseflow and stormflow differences in major-ion chemistry

The survey data segregate into two distinct patterns, which are associated with the level of streamflow and the residence time of water in the catchments. In May, July and September, discharge is essentially baseflow-dominated, and streams have high base cation and alkalinity concentrations. In November, January and March, discharge is stormflow-dominated, with lower base cation and alkalinity concentrations. The two behaviour patterns were further examined by using the major-ion chemistry of the 55 streams under 'baseflow' and 'stormflow' conditions (Figure 4.8). For the purpose of this exercise, 'baseflow' is represented by the lowest flow month (September) and 'stormflow' is represented by the highest flow month (November).

The base cation concentrations are higher under baseflow than stormflow conditions. This pattern is a reflection of the hydrochemical processes acting within the catchments. Since precipitation is much reduced during summer, little surface runoff occurs at this time and groundwater provides much of the stream flow. The water has had long contact times with the underlying bedrock, allowing chemical weathering of the rock. Thus, streamwater at baseflow has significant base cation concentrations.

Figure 4.8 - Mean major ion concentrations at baseflow (open bars) and stormflow (stippled bars) for the non-agricultural study streams.
NB. Baseflow is taken as the lowest monthly flow survey (Sept 1996) and stormflow is taken as the highest monthly flow survey (Nov 1996) during the sample period.
(Units are $\mu eq\ l^{-1}$, except silica, which is $\mu g\ l^{-1}$. Error bars are ± 1 S.E.)



The majority of the geological groups exhibit their lowest base cation and alkalinity concentrations during November (i.e. stormflow). The slightly elevated silica levels during November might suggest that an increase in weathering and base cation supply might be occurring (cf. Table 4.5). However, no concomitant increase in stream base cations is evident. Why? The volume of precipitation increases significantly during the winter months (brought about by high intensity rain events) and the water has shorter contact times with the bedrock. During these high-flow periods, washout of weathered ions as well as physical and chemical weathering may occur and the water may only flow through the top (base-depleted) soil layers before entering the stream. The result is a larger, but less concentrated, number of ions in the water. This 'base-rich' groundwater is subsequently mixed with a large amount of base-deficient rainwater causing flushes of acidic water or 'acid episodes' (UKAWRG, 1988). A stream's response to these acidic pulses is critical in determining its ability to sustain healthy biota populations and buffer acid precipitation (Whitehead *et al.*, 1988a). Alternatively, it may be because silica concentration is not a simple direct indicator of the rate of weathering in primary minerals because the stoichiometric ratio varies depending on the secondary phase of weathering (Section 1.2.1).

The stormflow concentration of nitrate is very similar to the baseflow concentration. This suggests a predominantly diffuse (catchment) source for the stormflow concentration,

such as fertilizer runoff (NRA, 1992a), or animal waste products (Ryden *et al.*, 1984). However, these mechanisms are normally more important in summer or autumn rather than occurring in winter but, in particularly dry years, it is possible for 50-60% of the annual nitrate loss to streamwater to be accounted for by winter rain events or stormflow (Burt and Arkell, 1987). The comparison of the precipitation and discharge during the study period with historical conditions suggested that this is a plausible explanation here, as the survey year was particularly dry.

4.3.2 Flow-weighted chemistry of Lake District streams and an assessment of the role of geology, land use, soil and atmospheric deposition

A version of this section has been published in the paper: GJP Thornton & NB Dise (1998). The influence of catchment characteristics, agricultural activities and atmospheric deposition on the chemistry of small streams in the English Lake District. *The Science of the Total Environment, Vol 216, p63-75.*

The ion concentrations of a stream fluctuate widely over time due to variations in discharge and / or seasonal influences (Harned *et al.*, 1981). These may mask the long-term trends actually occurring in the streams and spot samples of streamwater chemistry can therefore vary greatly over the period of one year. For example, during stormflow conditions large amounts of base-deficient rainwater are mixed with the base-rich groundwater causing flushes of acidic water (Section 4.3.1d). This changing hydrological regime results in a changing sensitivity over time to stresses, such as acid deposition or excess nitrogen runoff. With this in mind, water samples should be collected and analysed over a variety of hydrologic and seasonal conditions to integrate this variability. However, ion concentrations take no account of the amount of water passing through the system. This means two streams of differing size can record exactly the same ion concentrations yet have an order of magnitude difference in their fluxes.

Due to the heterogeneity of streamwater chemistry, on a temporal as well as spatial scale, the most sensible way of identifying trends in the chemical data is to weight the ion concentration using discharge. The 'flow-weighting' method gives the best estimate of the annual concentration of the ion from each stream by taking discharge into account. The annual flow-weighted concentration for each site was calculated using the following equation:

$$C_{fw} = \Sigma (C_i * Q_i) / \Sigma Q_i$$

where C_{fw} is the calculated flow-weighted concentration;
C_i is the measured concentration on the i^{th} trip;
Q_i is the measured streamflow on the i^{th} trip.

Using the annual flow-weighted concentrations, the variations in the stream chemistry of the 55 study catchments was assessed in relation to the catchment characteristics of geology, land use, soil and atmospheric deposition. The second phase of the stream chemistry work was undertaken in two stages: (i) Examining the inter-relationships within the data using a correlation matrix (Section 4.3.2a) and (ii) Examining the patterns in the chemical data using graphs categorised by the catchment characteristics (Section 4.3.2b).

a. *Correlations between the flow-weighted ion chemistry and catchment characteristics*

The annual flow-weighted chemical data and the catchment characteristics were examined using a correlation matrix (Table 4.12). The correlation matrix was used to identify any notable relationships and interactions within the data. The correlation coefficients that are statistically significant at the 1% level are shaded.

The majority of the chemical determinands have significant positive correlations with the other chemical determinands (ranging from 0.36 between chloride and magnesium to 0.89 between alkalinity and calcium). Significant correlations were found in all chemical constituents except: (1) between pH and sodium (-0.09), potassium (0.31), chloride (-0.07), nitrate (0.22) and sulphate (0.01); (2) between alkalinity and sodium (0.07), chloride (0.01) and sulphate (0.07); and (3) between silica and sodium (-0.01), potassium (0.27), chloride (0.01), nitrate (0.10) and sulphate (-0.08). In general, the base cations (calcium, magnesium and potassium) are strongly related with each other as well as alkalinity. In addition, sodium and chloride are also strongly related due to their natural chemical affinity in sea-salt, which is to be expected with a maritime region like the Lake District.

The majority of the chemical data was negatively correlated to Borrowdale Volcanic geology (%), ranging from -0.51 for potassium to -0.36 for nitrate. Significant correlations were not found for pH (-0.20) and silica (-0.25). The majority of the chemical data was positively correlated to Silurian Slate geology (%), ranging from 0.63 for calcium to 0.37 for magnesium. Significant correlations were not found for sodium (0.23), chloride (0.31) and sulphate (0.35). Only pH (-0.36) was negatively correlated to Skiddaw Slate geology (%). Significant correlations were not found between all the chemical data and the Granite (%) and Mixed Lithology (%) geology categories, and the majority of the chemical data and the Skiddaw Slate group. In general, the chemical data exhibited moderate relationships with the Borrowdale Volcanics, whereas calcium, potassium and alkalinity concentrations were strongly related to the percentage Silurian Slate geology.

Table 4.12 – A correlation matrix showing correlations between mean annual flow-weighted major ion concentrations in the stream and catchment characteristics for the 55 study catchments. (Annual flow-weighted data (N=55). Shaded values ($r > 0.354$) are statistically significant at the 1% level ($p < 0.01$)).

	pH	Na	Mg	Ca	K	Cl	NO_3	SO_4^{2-}	Alk	SiO_2	BVG	SKS	SIL	MIX	GR	UPL	FOR	AGR	D1	D2	D3	D4	D5	D6	D7	THP	THI	GLY
Na	-0.09																											
Mg	**0.40**	**0.59**																										
Ca	**0.67**	0.34	**0.66**																									
K	0.31	**0.51**	**0.69**	**0.77**																								
Cl	-0.07	**0.80**	**0.36**	**0.42**	**0.57**																							
NO_3	0.22	**0.47**	**0.49**	**0.76**	**0.88**	**0.61**																						
SO_4^{2-}	0.00	**0.60**	**0.39**	**0.43**	**0.47**	**0.73**	**0.48**																					
Alk	**0.77**	0.07	**0.63**	**0.89**	**0.62**	0.08	**0.52**	0.07																				
SiO_2	**0.54**	-0.01	**0.37**	**0.40**	0.27	0.00	0.10	-0.08	**0.58**																			
BVG	-0.20	**-0.37**	**-0.44**	**-0.48**	**-0.51**	**-0.39**	**-0.36**	**-0.43**	**-0.38**	-0.25																		
SKS	**-0.36**	0.07	0.03	-0.13	-0.04	0.12	-0.12	0.16	-0.15	-0.11	-0.34																	
SIL	**0.44**	0.23	**0.37**	**0.63**	**0.57**	0.31	**0.49**	0.35	**0.53**	**0.38**	**-0.83**	-0.16																
MIX	0.11	0.25	0.31	0.04	0.00	-0.11	-0.08	0.05	0.02	-0.13	-0.25	-0.07	0.12															
GR	-0.20	0.32	0.09	-0.20	-0.01	0.28	-0.07	0.05	-0.21	-0.11	-0.01	-0.08	-0.17	-0.07														
UPL	**-0.48**	-0.25	**-0.39**	**-0.69**	**-0.61**	-0.32	**-0.56**	-0.31	**-0.64**	**-0.52**	**0.68**	0.12	**-0.86**	0.09	0.17													
FOR	0.10	0.23	-0.02	0.18	0.06	0.30	0.07	**0.38**	0.07	0.24	-0.35	-0.07	**0.45**	-0.07	-0.08	**-0.57**												
AGR	**0.51**	0.13	**0.49**	**0.71**	**0.71**	0.17	**0.63**	0.09	**0.73**	**0.45**	**-0.57**	-0.10	**0.71**	-0.06	-0.15	**-0.80**	-0.05											
D1	-0.19	0.00	0.09	-0.06	0.01	-0.09	-0.07	-0.13	0.09	0.06	-0.17	**0.57**	-0.12	-0.05	-0.06	0.01	-0.06	0.02										
D2	0.02	0.06	0.05	-0.08	0.00	0.11	-0.11	0.08	-0.06	0.18	0.02	0.28	-0.14	-0.06	-0.07	0.14	-0.06	-0.13	-0.05									
D3	**0.38**	0.17	**0.41**	**0.62**	**0.66**	0.22	**0.61**	0.09	**0.58**	0.34	**-0.55**	-0.10	**0.68**	-0.02	-0.11	**-0.65**	-0.11	**0.87**	-0.07	-0.09								
D4	-0.24	0.27	0.05	-0.21	-0.03	0.25	-0.07	0.07	-0.24	-0.10	-0.13	0.28	-0.14	-0.06	**0.59**	0.14	-0.07	-0.13	-0.05	-0.06	-0.09							
D5	0.02	0.07	-0.13	-0.05	-0.04	0.13	-0.02	0.15	-0.10	0.03	-0.17	-0.12	0.26	-0.11	0.06	-0.30	**0.57**	-0.05	-0.09	-0.11	-0.17	-0.11						
D6	0.22	-0.28	0.16	0.01	-0.15	**-0.43**	-0.22	-0.13	0.13	0.01	0.22	-0.18	-0.18	0.33	-0.09	0.27	-0.19	-0.19	-0.13	-0.16	-0.26	-0.16	-0.30					
D7	-0.35	-0.06	**-0.46**	-0.26	-0.30	0.03	-0.09	-0.08	**-0.38**	**-0.36**	**0.46**	-0.16	-0.35	-0.15	-0.12	0.31	-0.11	-0.30	-0.11	-0.14	-0.22	-0.14	-0.26	**-0.39**				
THP	0.23	0.32	**0.42**	**0.62**	**0.66**	**0.39**	**0.60**	**0.36**	**0.50**	0.18	**-0.77**	0.33	**0.66**	0.10	-0.13	**-0.62**	0.08	**0.70**	0.06	0.03	**0.69**	0.00	-0.05	-0.22	-0.29			
THI	0.24	-0.05	-0.02	0.22	0.09	-0.02	0.20	-0.09	0.22	0.09	0.16	-0.22	-0.04	-0.11	0.04	-0.07	-0.19	0.23	-0.18	-0.25	0.21	-0.07	-0.26	0.06	0.24	0.30		
GLY	0.20	-0.03	0.26	0.14	0.13	-0.02	-0.03	0.02	0.21	0.23	-0.25	0.03	0.27	-0.01	-0.06	-0.12	-0.09	0.20	0.24	-0.03	0.14	-0.09	-0.14	0.11	-0.14	0.10	-0.05	
PTY	-0.33	-0.20	**-0.39**	**-0.59**	**-0.56**	-0.27	**-0.51**	-0.23	**-0.52**	-0.25	**0.58**	-0.16	**-0.55**	-0.02	0.10	**0.52**	0.05	**-0.67**	-0.05	0.09	**-0.63**	0.06	0.18	0.10	0.17	**-0.88**	**-0.59**	**-0.39**

The majority of the chemical data was negatively correlated to upland vegetation (%), ranging from -0.69 for calcium to -0.39 for magnesium. Significant correlations were not found for sodium (-0.25), chloride (-0.32) and sulphate (-0.32). The majority of the chemical data was positively correlated to agriculture (%), ranging from 0.73 for alkalinity to 0.45 for silica. Significant correlations were not found for sodium (0.13), chloride (0.17) and sulphate (0.09). Sulphate (0.38) was positively correlated to forested land (%). On the whole, calcium, potassium and alkalinity concentrations are strongly related to percentage upland vegetation and agriculture.

The majority of the chemical data was positively correlated to % deposition load 3 (DEP 3), ranging from 0.66 for potassium to 0.38 for pH. Significant correlations were not found for sodium (0.17), chloride (0.22), sulphate (0.09) and silica (0.34). Chloride (-0.43) was negatively correlated to % deposition load 6 (DEP 6), whilst magnesium (-0.46), alkalinity (-0.38) and silica (-0.36) were negatively correlated to % deposition load 7 (DEP 7). Significant correlations were not found between the chemical data and the other four deposition loads (DEP 1, 2, 4 and 5). Overall, the relationships between the chemical data and % deposition loads are weak. The strongest relationships with the chemical data, particularly calcium, potassium and nitrate concentrations, were with % deposition load 3.

The majority of the chemical data was positively correlated to % thick, porous soil (THP), ranging from 0.66 for potassium to 0.36 for sulphate. Significant correlations were not found for pH (0.23), sodium (0.32) and silica (0.18). Half the chemical data was negatively correlated to % peaty soil (PTY), ranging from -0.59 for calcium to -0.39 for magnesium. Significant correlations were not found for pH (-0.33), sodium (-0.20), chloride (-0.27), sulphate (-0.23) and silica (-0.25). Significant correlations were not found between the chemical data and % thin, impermeable soil (THI) and % gleyed soil (GLY). Generally, calcium and potassium concentrations were strongly related to % THP and PTY soil.

There were some strong correlations between the chemical data, most noticeably calcium, potassium, nitrate and alkalinity concentrations, and the catchment characteristics (Table 4.11). As found in the individual trip data (Section 4.3.1a), the chemical data was negatively correlated with Borrowdale Volcanic geology, upland vegetation, DEP 7 and PTY soil. These four catchment characteristics also exhibit strong positive correlations with each other, and therefore might be found together in stream catchments. The chemical data was positively correlated with Silurian Slate geology, agriculture, DEP 3 and THP soil. Again, the catchment characteristics exhibit strong positive correlations with each other suggesting they might be found together in stream catchments.

b. Examining flow-weighted ion chemistry in relation to catchment characteristics[#]

Variations in the mean annual flow-weighted ion chemistry, alkalinity, silica and stream discharge were examined in relation to the geology, land use, soil and the atmospheric deposition of the sites. The streams were examined in this way to establish overall behaviour differences in the individual groups.

GEOLOGY & LAND USE

The mean annual flow-weighted chemical data were categorised according to rock type and land use (Figure 4.9). The Silurian Slates were divided again into two sub-groups because of the strong positive correlation found between Silurian Slates and agriculture on the correlation matrix (Table 4.12).

Categorising the chemical data by rock type and land use suggests that some ions exhibit large differences between the groups, whilst others show low variability across the groups (Figure 4.9). For example, the calcium, nitrate and alkalinity concentrations (as well as discharge) show a high degree of variability across the categories. In contrast, pH, sodium, magnesium, chloride, sulphate and silica concentrations exhibit less distinct differences between the categories.

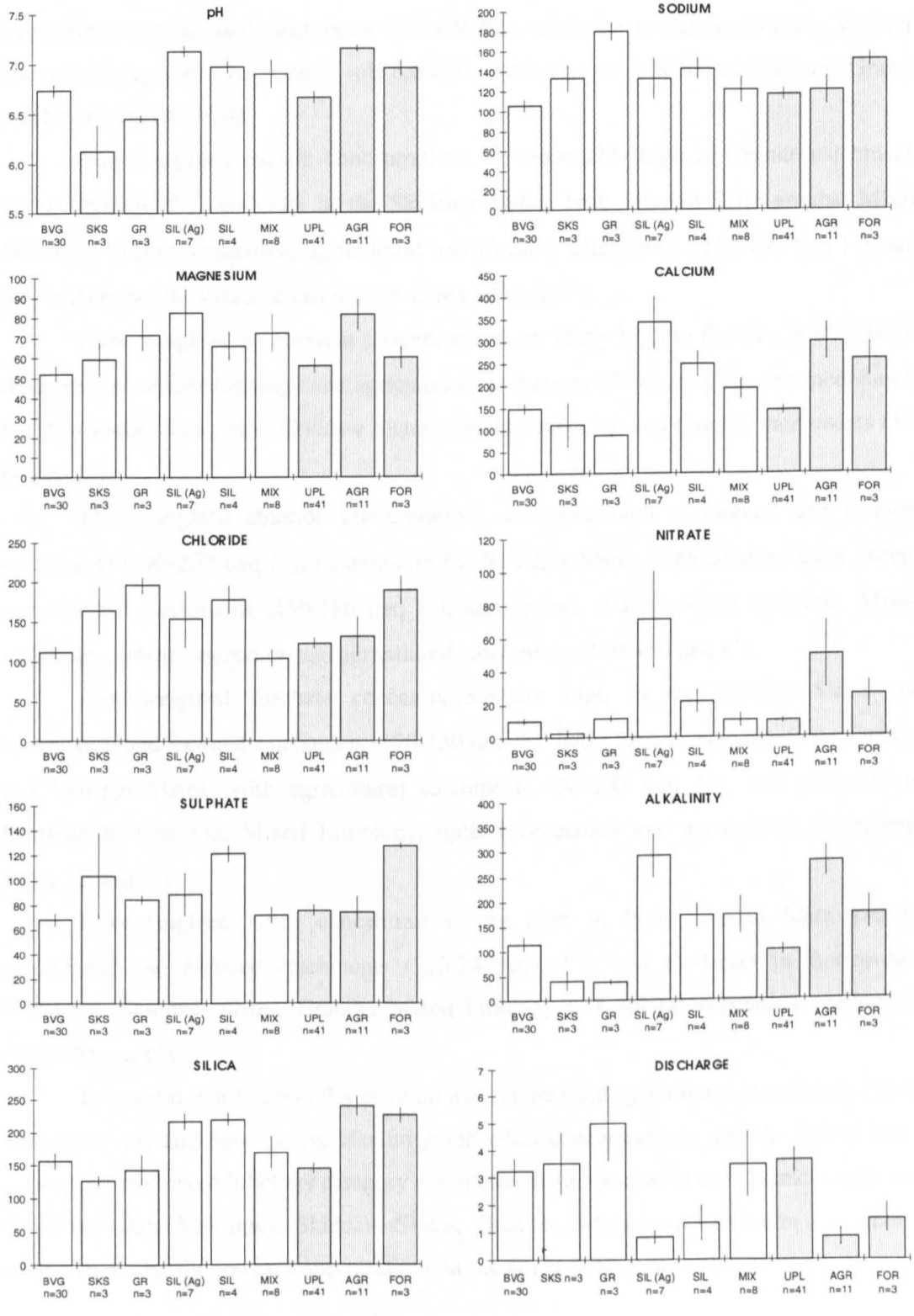
Flow-weighted calcium concentrations are high in the Silurian Slates (with agriculture) and agricultural catchments (300-350 $\mu eq\ l^{-1}$), moderately high in the Silurian Slates (no agriculture), Mixed lithology and forested catchments (200-250 $\mu eq\ l^{-1}$), low in Borrowdale Volcanic and upland vegetation catchments (circa 150 $\mu eq\ l^{-1}$), and very low in Skiddaw Slate and Granite catchments (< 100 $\mu eq\ l^{-1}$).

Flow-weighted nitrate concentrations are high in the Silurian Slates (with agriculture) and agricultural catchments (50-70 $\mu eq\ l^{-1}$), moderately low in the Silurian Slates (no agriculture) and forested catchments (circa 20 $\mu eq\ l^{-1}$), and very low in Borrowdale Volcanic, Skiddaw Slate, Granite, Mixed lithology and upland vegetation catchments (< 10 $\mu eq\ l^{-1}$).

Flow-weighted alkalinity is high in the Silurian Slates (with agriculture) and agricultural catchments (circa 300 $\mu eq\ l^{-1}$), moderately high in the Silurian Slates (no agriculture), Mixed lithology and forested catchments (circa 150 $\mu eq\ l^{-1}$), low in Borrowdale Volcanic and upland vegetation catchments (circa 100 $\mu eq\ l^{-1}$), and very low in Skiddaw Slate and Granite catchments (< 50 $\mu eq\ l^{-1}$).

[#] **NOTE:** The flow-weighted chemical data for potassium (K^+) is not examined because the concentration of this ion is nearly always very low (84 % of flow-weighted concentrations are below 5 $\mu eq\ l^{-1}$), and data for phosphate (PO_4^-) and ammonium (NH_4^+) are not examined because these two ions concentrations are always below the detection limit.

Figure 4.9 - Mean annual flow-weighted major ion concentrations of streams in the study categorised by rock type (open bars) and land use (stippled bars).
(Units are μeq l^{-1}, except pH, silica (μg l^{-1}) and mean discharge (m^3 sec^{-1}). Error bars are ± 1 S.E.)
Key: BVG – Borrowdale Volcanics; SKS – Skiddaw Slates; GR – Granite; SIL (Ag) – Silurian Slates with agriculture; SIL – Silurian Slates no agriculture; MIX – Mixed Lithology; UPL – Upland vegetation; AGR – Agriculture; FOR – Forested.



In this study, mean discharge is high in the Granite catchments (circa 5 $m^3 sec^{-1}$), moderate in the Borrowdale Volcanics, Skiddaw Slates, Mixed Lithology and upland vegetation catchments (circa 3 $m^3 sec^{-1}$), and low in both Silurian Slate groups, agricultural and forested catchments (circa 1 $m^3 sec^{-1}$).

Flow-weighted pH is fairly high in both Silurian Slate groups, Mixed lithology, agricultural and forested catchments (pH 6.9-7.2), moderate in the Borrowdale Volcanic and upland vegetation catchments (pH 6.6-6.8), and fairly low in Skiddaw Slate and Granite catchments (pH 6.1-6.4).

Flow-weighted sodium concentrations are reasonably high in Granite catchments (circa 180 $\mu eq\ l^{-1}$), moderate in the Skiddaw Slates, both Silurian Slate groups, Mixed lithology, upland vegetation, agricultural and forested catchments (120-150 $\mu eq\ l^{-1}$), and low in Borrowdale Volcanic catchments (circa 100 $\mu eq\ l^{-1}$).

Flow-weighted magnesium concentrations are fairly high in Granite, both Silurian Slate groups, Mixed lithology and agricultural catchments (70-80 $\mu eq\ l^{-1}$), and moderate in the Borrowdale Volcanics, Skiddaw Slates, upland vegetation and forested catchments (50-60 $\mu eq\ l^{-1}$).

Flow-weighted chloride concentrations are quite high in Granite and forested catchments (190-200 $\mu eq\ l^{-1}$), moderate in the Skiddaw Slates, both Silurian Slate groups and forested catchments (150-180 $\mu eq\ l^{-1}$), and lowest in Borrowdale Volcanic, Mixed Lithology, upland vegetation and agricultural catchments (100-130 $\mu eq\ l^{-1}$).

Flow-weighted sulphate concentrations are high in the Silurian Slates (no agriculture) and forested catchments (120-130 $\mu eq\ l^{-1}$), fairly high in Skiddaw Slate, Granite and Silurian Slates (with agriculture) catchments (90-100 $\mu eq\ l^{-1}$), and moderate in Borrowdale Volcanic, Mixed Lithology, upland vegetation and agricultural catchments (circa 70 $\mu eq\ l^{-1}$).

Flow-weighted silica concentrations are high in both Silurian Slate groups, agricultural and forested catchments (220-240 $\mu eq\ l^{-1}$), and moderate in Borrowdale Volcanics, Skiddaw Slates, Granite, Mixed lithology and upland vegetation catchments (120-170 $\mu eq\ l^{-1}$).

In general, the Silurian Slates (with agriculture) and agricultural catchments record the highest pH and base cation, alkalinity and silica concentrations, and the lowest mean discharges; the mixed lithology category are intermediate for most of the chemical data; and the Borrowdale Volcanics, Skiddaw Slates, Granite and upland vegetation catchments tended to record the lowest concentrations in the study period, and have the highest mean

discharges. However, if the streams draining the Silurian Slates were considered as a single geological category, a wide range in the concentrations of major ions and alkalinity would have occurred. As the majority of the agriculturally-dominated catchments occur in this group, the large range in concentrations are strongly related to the presence or absence of agricultural land use. Therefore, by splitting the group into 'with agriculture' and 'with no agriculture', the major influence that agriculture imparts on stream chemistry has been highlighted.

Calcium, nitrate and alkalinity concentrations are significantly higher in the 'with agriculture' group (Figure 4.9). This suggests that agriculture is responsible for the addition of significant amounts of calcium, nitrate and alkalinity into the streamwater. However, as the silica concentrations are very similar for both Silurian Slate groups (Figure 4.9), it is fair to suggest that the increased concentrations of calcium and alkalinity in the 'with agriculture' group are derived from processes other than weathering. For example, widespread artificial liming of Lake District stream catchments has occurred since the turn of the century (Parry *et al.*, 1982).

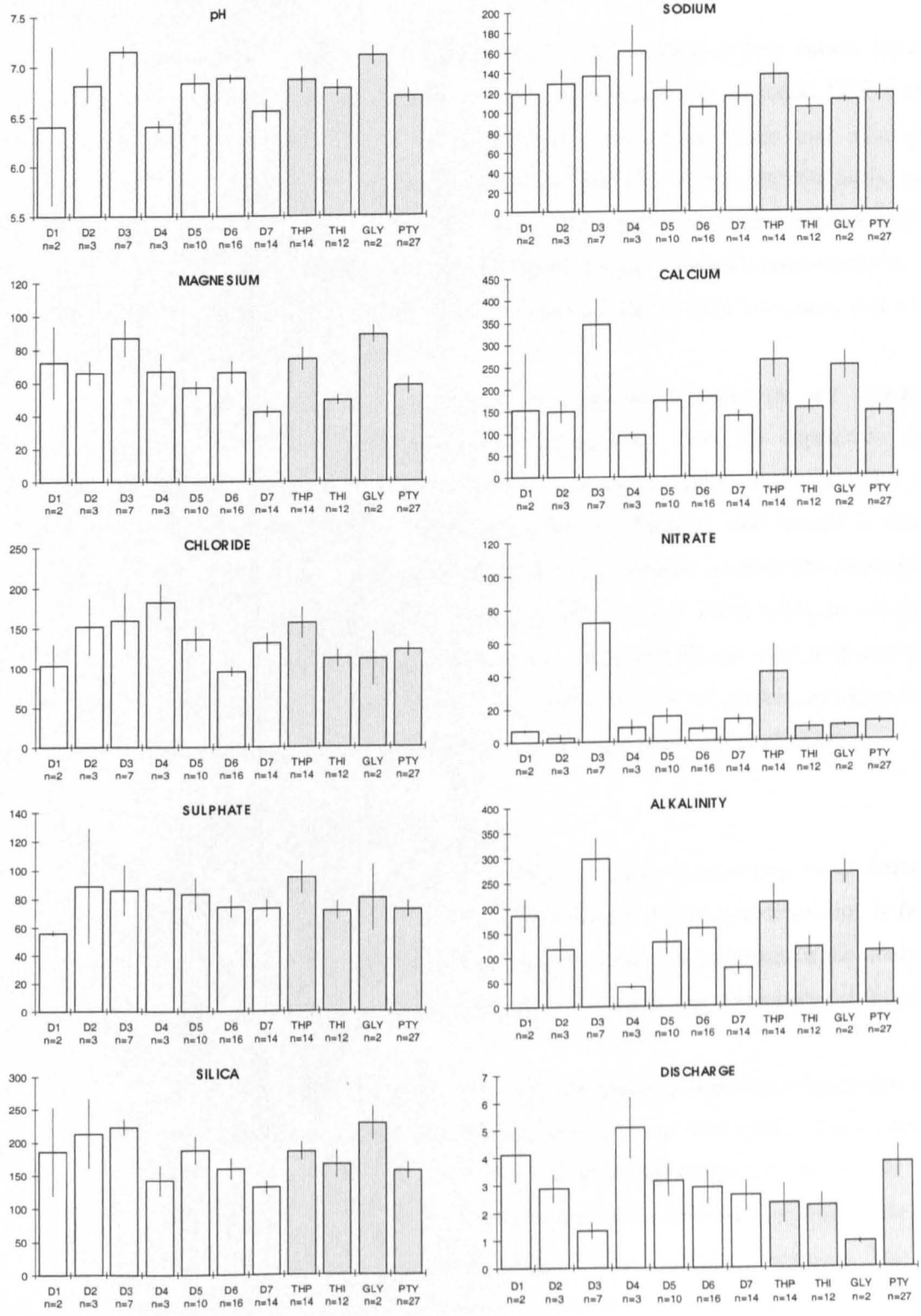
ATMOSPHERIC DEPOSITION & SOILS

The mean annual flow-weighted chemical data were categorised according to atmospheric deposition load and soil type (Figure 4.10). Calcium, nitrate and alkalinity concentrations (as well as discharge) show a high degree of variability across the categories, pH and magnesium concentrations exhibit a moderate amount of variability, whilst sodium, chloride, sulphate and silica concentrations display low variability. Relationships between streamwater chemistry and soils will be discussed first and then deposition will be briefly discussed.

Flow-weighted calcium concentrations are fairly high in the THP and GLY soil catchments (circa 250 $\mu eq\ l^{-1}$) and low in THI and PTY soil catchments (150-175 $\mu eq\ l^{-1}$). Flow-weighted nitrate concentrations are moderate in THP soil catchments (circa 40 $\mu eq\ l^{-1}$) and low in THI soil, GLY soil and PTY soil catchments (< 10 $\mu eq\ l^{-1}$). Flow-weighted alkalinity is high in GLY soil catchments (circa 250 $\mu eq\ l^{-1}$), moderately high in THP soil catchments (circa 200 $\mu eq\ l^{-1}$), and low in THI soil and PTY soil catchments (100-150 $\mu eq\ l^{-1}$). In this study, mean discharge is high in PTY soil catchments (circa 3.5 $m^3\ sec^{-1}$), moderate in THP soil and THI soil catchments (circa 2 $m^3\ sec^{-1}$), and low in GLY soil catchments (< 0.5 $m^3\ sec^{-1}$).

Figure 4.10 - Mean annual flow-weighted major ion concentrations of streams in the study categorised by deposition loading (open bars) and soil type (stippled bars).

(Units are μeq l^{-1}, except pH, silica (μg l^{-1}) and mean discharge (m^3 sec^{-1}). Error bars are ± 1 S.E.)
Key: D1 to D7 – Deposition loads 1 to 7; THP – Thick & Porous Soil; THI – Thin & Impermeable Soil; GLY – Gleyed Soil; PTY – Peaty Soil.



Flow-weighted pH is fairly high in GLY soil catchments (circa pH 7.2) and moderate in THP soil, THI soil and PTY soil catchments (pH 6.7-6.9). Flow-weighted magnesium concentrations are fairly high in GLY soil catchments (circa 90 $\mu eq\ l^{-1}$), moderate in THP soil and PTY soil catchments (60-75 $\mu eq\ l^{-1}$), and low in THI soil catchments (< 50 $\mu eq\ l^{-1}$).

In general, DEP 3 and GLY soil catchments have the highest base cation, nitrate, silica and alkalinity concentrations, and the lowest mean discharges, whereas DEP 4 and DEP 7 catchments tend to exhibit the lowest pH, base cation, silica and alkalinity concentrations. In addition, catchments underlain by THP soil tend to exhibit fairly high concentrations for the majority of the chemical determinands. Although sulphate seems relatively uniform for the majority of the groups, unlike nitrate it shows a relationship to the flux of the ion in deposition (i.e. lowest sulphate concentration is found in streams receiving the lowest annual sulphate deposition).

It is fair to say that the patterns in the deposition categories are probably confounded by the effects of land use, soil and geology, thus the deposition data presumably doesn't really reflect the effects of deposition alone. For example, the association between DEP 3 and elevated base cations, alkalinity and nitrate is likely spurious as the majority of the agriculture-dominated catchments receive this deposition load (a fact identified by the strong positive relationship found in Table 4.12). In addition, the data from the 20 x 20km atmospheric deposition grids should be used with extreme caution at the catchment scale. Therefore, the Cl balance method of calculating deposition was also used to assess the role of atmospheric deposition on streamwater chemistry.

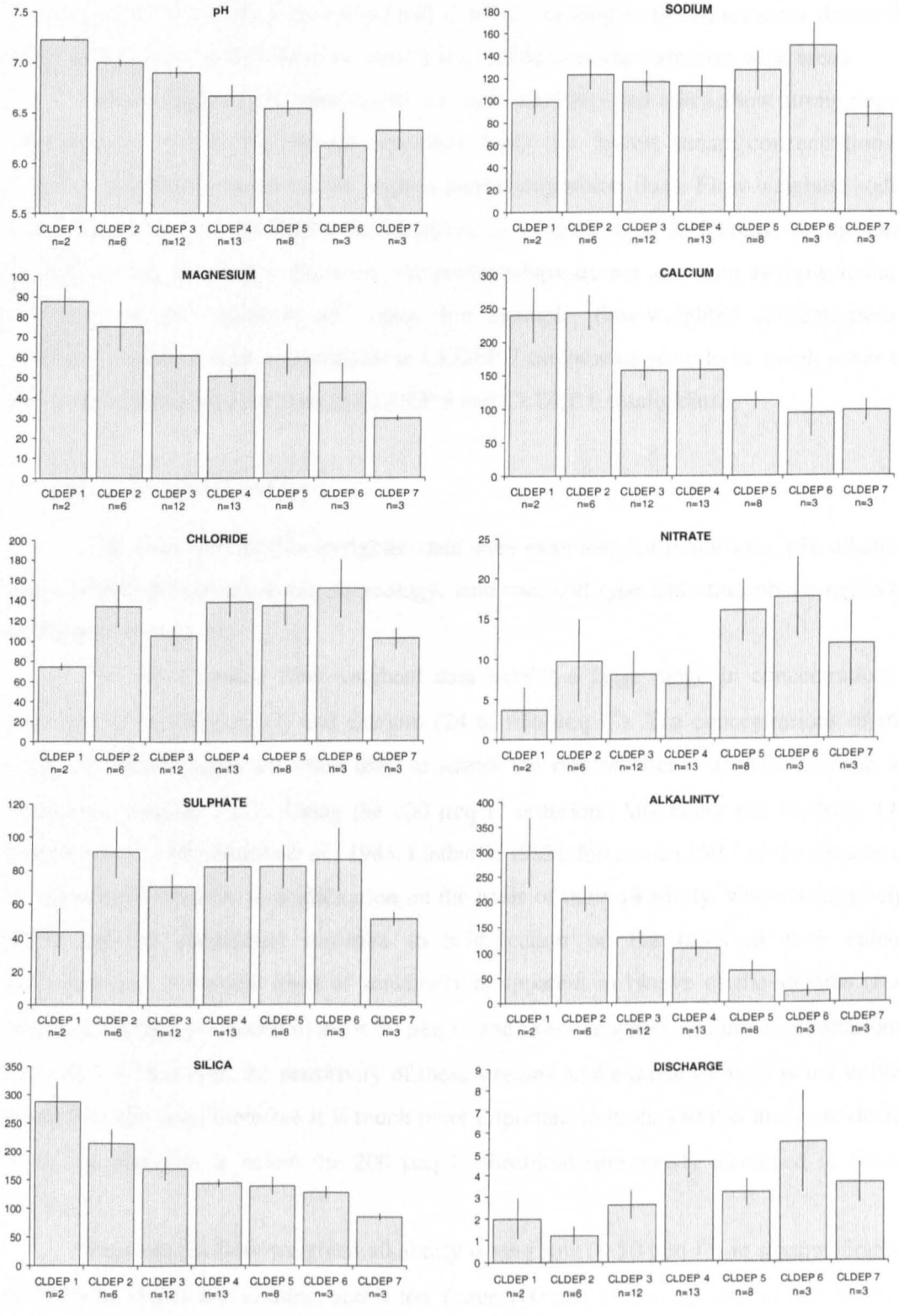
CL BALANCE ATMOSPHERIC DEPOSITION

The mean annual flow-weighted chemical data was categorised according to Cl balance deposition loads (Figure 4.11). The method of calculating the Cl balance deposition is fully explained in Section 4.2.2. The agricultural catchments were not included in the analysis because of the major influence agriculture impinges on streamwater chemistry (cf. Figures 4.5 to 4.7 and Figure 4.9).

Much clearer patterns are found using the Cl balance deposition loads but the patterns may reflect the recalculation of rain chemistry or they may reflect real patterns. Despite the method being a common way of calculating deposition (cf. Jenkins *et al.*, 1997), a possible flaw in the logic is that the catchment deposition is based on the concentration of ions in streamwater which contain other catchment artefacts. The Cl balance deposition load may therefore be inherently biased thus making it difficult to assess

Figure 4.11 - Mean annual flow-weighted major ion concentrations of streams in the study categorised by Cl balance deposition loading.

(Units are μeq l^{-1}, except pH, silica (μg l^{-1}) and mean discharge ($m^3 sec^{-1}$) Error bars are ± 1 S.E.)
Key: CLDEP1 to CLDEP7 – Cl balance deposition loads 1 to 7.



whether this method actually produces the patterns, or whether it merely highlights the patterns that were already there (i.e. circular argument). To independently test this assumption, a raingauge would have to be installed at every catchment for the duration of the study period, which is an impractical solution. As long as the conclusions drawn from these patterns err on the side of caution, it is possible to extrapolate over wide areas.

Flow-weighted pH, magnesium, calcium, alkalinity and silica show strong negative relationships with the Cl balance deposition loads (i.e. lowest stream concentrations are found in catchments receiving the highest annual deposition flux). Flow-weighted sodium, chloride, nitrate and sulphate concentrations, in contrast, tend to increase as the annual deposition flux gets larger. However, the relationships are not as strong as those found for pH, base cations, alkalinity and silica. For example, flow-weighted concentrations of sodium, chloride, nitrate and sulphate in CLDEP 7 catchments seem to be much lower than the concentrations of these ions in CLDEP 5 and CLDEP 6 catchments.

c. Discussion and Summary

The mean annual flow-weighted data were examined for major ions, pH, alkalinity, silica and discharge in relation to geology, land use, soil type and atmospheric deposition by Figures 4.9 to 4.11.

The mean annual flow-weighted data exhibit a large range in concentrations of alkalinity (2 to 452 $\mu eq\ l^{-1}$) and calcium (24 to 656 $\mu eq\ l^{-1}$). The concentrations of these chemical determinands are often used to assess the risk of stream acidification via acid deposition (Section 1.1.2). Using the 200 $\mu eq\ l^{-1}$ criterion (Altschuller and McBean, 1979; Hendrey *et al.*, 1980; Haines *et al.*, 1983; Linthurst, 1983), forty-one (75%) of the streams can be considered sensitive to acidification on the basis of their alkalinity, whereas thirty-eight (69%) can be considered sensitive to acidification on the basis of their calcium concentrations. A critical level of sensitivity is apparent in twelve of the streams (flow-weighted alkalinity concentrations < 50 $\mu eq\ l^{-1}$ and flow-weighted calcium concentrations < 100 $\mu eq\ l^{-1}$). However, the sensitivity of these streams or the threat to biota is not uniform throughout the year, therefore it is much more important to biota survival and reproduction when the alkalinity is below the 200 $\mu eq\ l^{-1}$ threshold (previously discussed in Section 4.3.1c).

Mean annual flow-weighted alkalinity is very low (< 50 $\mu eq\ l^{-1}$) in streams draining the Skiddaw Slates and Granite, and is low (circa 100 $\mu eq\ l^{-1}$) for the Borrowdale Volcanic stream catchments (Figure 4.9). These are also the catchments with the lowest silica levels,

which might suggest lower weathering rates (cf. Table 4.5). Supporting this, whole-rock weathering patterns suggest that little or no weathering occurs in Skiddaw Slate samples, but weathering varies in samples from the Borrowdale Volcanic Group (Section 3.5.3). The heterogeneity in water chemistry found in streams draining the Borrowdale Volcanics (e.g. flow-weighted alkalinity ranges between 1 and 300 $\mu eq\ l^{-1}$) might be accounted for by the variability in weathering patterns (or stoichiometric ratios) of this bedrock (cf. Table 4.5 and Section 1.2.1). In addition, alkalinity is low (circa 100 $\mu eq\ l^{-1}$) in catchments receiving DEP 7, and relatively low (100-150 $\mu eq\ l^{-1}$) in catchments underlain by THI and PTY soils (Figure 4.10). These patterns suggest that low alkalinity streamwater in the Lake District is due to: (a) low base cation resupply via weathering of the bedrock (supported by whole-rock weathering patterns), (b) short residence times in thin soils, (c) longer residence times in thick, acidic soils, and/or (d) inputs of anions from acid precipitation.

In contrast, mean annual flow-weighted alkalinity is relatively high (circa 300 $\mu eq\ l^{-1}$) in the Silurian Slates (with agriculture) and agricultural catchments, and also is high (200-250 $\mu eq\ l^{-1}$) in catchments underlain by THP and GLY soil (Figures 4.9 and 4.10). These are also the catchments with the highest silica levels, which might suggest higher weathering rates (cf. Table 4.5 and Section 1.2.1). Whole-rock weathering patterns suggest that large amounts of weathering occur in Silurian Slate samples (Section 3.5.3), which supports this hypothesis.

Many upland areas in the Lake District have been subject to land management. Around 10% of rough pasture has been converted to farmland since the turn of the century (Parry *et al.*, 1982), thus raised alkalinity and base cation concentrations in agriculture-dominated catchments are probably the result of historical liming. Although widespread liming projects ceased in the late 1970s due to a change in agricultural policy, local liming still occurs. Therefore, high alkalinity streamwater in the Lake District is likely to be due to (a) high base cation resupply from more easily-weathered bedrock (supported by silica and whole-rock weathering patterns), (b) enhanced cation exchange due to higher residence times of water in thicker soils, and/or (c) additional influx of base cations from land improvement including conversion to agriculture and liming (supported by results of Moorland Change Project Programme – i.e. Parry *et al.*, 1982).

Nitrate concentrations are greatly enhanced (40-70 $\mu eq\ l^{-1}$) in Silurian Slates (with agriculture) and agricultural catchments, and in catchments receiving DEP 3 and underlain by THP soil (Figures 4.9 and 4.10). Most of the agricultural catchments occur on THP soil and receive DEP 3, suggesting these variables are strongly inter-related (Table 4.12). It is likely that the effects of agriculture itself, rather than soil type or deposition, exert the main

influence on water chemistry in this case. Agricultural land in the Lake District tends to animal grazing rather than crop producing (Section 2.2.4), therefore, the elevated nitrate levels in these categories are probably due to sheep waste being leached into surface waters from catchment soils rather than fertiliser runoff. Supporting this, it has been found that Danish streams draining moorland catchments had a significantly lower pH, alkalinity and nutrient content than similar land use used for animal farming (Rebsdorf *et al.*, 1991).

A trend of elevated sulphate (circa 120 $\mu eq\ l^{-1}$) in Silurian Slate (no agriculture) and forested catchments was evident (Figure 4.9). Diatom evidence from Scotland points to an increase in acidification following afforestation (Kreiser *et al.*, 1990). Further evidence from paired catchment studies in Wales indicates that forested streams are more acidic than grassland streams even if the bedrock and soils are similar (Ormerod *et al.*, 1989). Neal *et al.* (1992b,c) suggest that preferential scavenging of acidic atmospheric compounds could explain the increased acidity of the surface water in forested catchments. Likewise, the trend found for elevated sulphate in this study could be attributed to the scavenging of atmospheric sulphur by trees.

Although the forestry cover in the Lake District is currently relatively small (circa 15%), the Forestry Commission is responsible for several ongoing large-scale afforestation projects. To date, several large areas of pristine moorland (as much as 12% of the total amount) have been converted to coniferous plantations since the 1940s (Nature-Conservancy-Council, 1987). Therefore, this may have major implications for Lake District streams in the future.

In this study, catchment modification by agricultural land use seems to add large amounts of alkalinity, base cations and nitrate, approximately doubling alkalinity and tripling nitrate concentrations where agricultural use is high (Figure 4.9). Thus, conversion of pristine catchments to agriculture may play a large role in the modification of streamwater chemistry – and is therefore assessed further in the 'Space as a surrogate for time' aspect of the thesis (Section 4.3.4).

In far as the geological groups are concerned, major ion concentrations tend to be highest on the Silurian Slates, particularly the base cation concentrations (Figure 4.9). This is probably due to preferential weathering of the less resistant bedrock, which is supported by the higher concentrations of silica in streamwater and the weathering patterns derived from the whole-rock chemistry work (Section 3.5.3). The Silurian Slates have a high proportion of mobile elements like calcium, magnesium, sodium and potassium, and a low proportion of immobile elements like silica, iron and aluminium in the whole-chemistry (Section 3.3.2), thus making weathering easier.

In contrast, major ion concentrations (particularly the base cation concentrations) tend to be lowest on the Skiddaw Slates and Granite, and to a lesser extent on the Borrowdale Volcanics (Figure 4.9). This is probably due to low rates of weathering from these bedrocks, which is supported by the lower concentrations of silica in streamwater and the lack of weathering patterns derived from the whole-rock chemistry work (Section 3.5.3). The Skiddaw Slates have a high proportion of immobile elements like silica, iron and aluminium, and a low proportion of mobile (i.e. weatherable) elements like calcium, sodium and potassium in the whole-chemistry (Section 3.3.2), thus making it resistant to weathering. The Borrowdale Volcanics have a very heterogeneous chemistry, which covers the whole spectrum of volcanic rock geochemistry (Section 3.3.2), thus the amount of weathering varies greatly. As previously discussed (Section 3.5.3), the weathering pattern differences don't apportion themselves to different rock types within the Borrowdale Volcanics. One of the explanations suggested that the area receives several diverse acid deposition loads and this might lead to different weathering rates. This is discussed further in Section 4.3.3.

4.3.3. Using geochemical data as an aid for investigating the catchment contributions to streamwater chemistry

This section describes the 'catchment contribution' to streamwater chemistry resulting from two different methods. The first is a new method, which takes geochemical data from weathered and fresh rocks to determine whether different weathering patterns occur under different loads of atmospheric acid deposition (Section 4.3.3a). The second uses an established method (for example, Edmunds and Key, 1996), where the effects of rainfall are removed from streamwater chemistry using chloride, thus allowing only the water-rock interactions and human influences to be assessed (Section 4.3.3b).

a. Base cation resupply from rocks and the effects of acid deposition

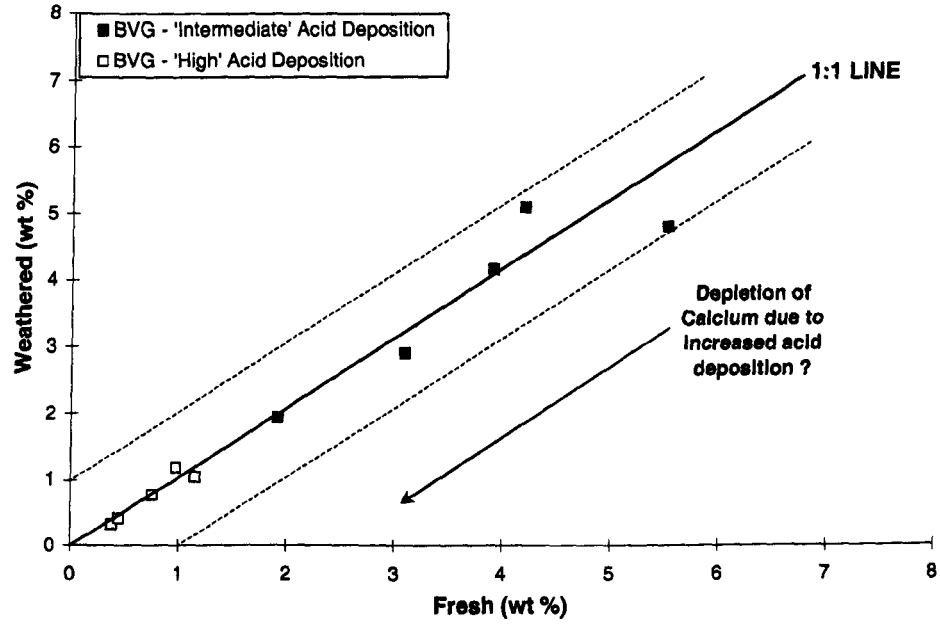
As previously discussed, the Borrowdale Volcanic Group has a heterogeneous chemistry, both for streamwater (Section 4.3.1 and 4.3.2) and whole-rock samples (Section 3.3.2). This method assesses whether the several diverse acid deposition loads received by the area explain why the weathering rates, and consequently streamwater chemistry, of the Borrowdale Volcanic rocks are different.

Firstly, weathered and fresh calcium compositions of ten Borrowdale Volcanic rock samples from low alkalinity (i.e. $< 50\ \mu eq\ l^{-1}$) stream catchments were plotted against each

other (Figure 4.12). Using the UK Critical Loads deposition grids, five of the samples received a 'high' acid deposition load (Nitrate 1.0 keq/ha/yr^{-1} and Sulphate 2.3 keq/ha/yr^{-1}) whilst the other five samples received an 'intermediate' acid deposition load (Nitrate 0.5-0.6 keq/ha/yr^{-1} and Sulphate 1.3-1.6 keq/ha/yr^{-1}).

Sites receiving intermediate deposition loads have a higher calcium composition (between 2 and 6 %) than the sites receiving the high deposition loads (mostly < 1%). As the two groups aren't apportioned on the basis of rock type and the age difference between the rock types is negligible, the contrasting acid deposition loads may have led to a depletion of the rocks calcium composition near the surface. The rock samples show very little movement away from the 1:1 line. This suggests that little or no preferential leaching of calcium is occurring from the obviously weathered parts of the rock and may help to explain the low alkalinity of the streams draining these catchments.

Figure 4.12 - Diagram comparing the calcium compositions of 10 Borrowdale Volcanic Group rock samples under varying acid deposition loadings.
('Intermediate' acid load = Nitrate 0.5-0.6 keq/ha/yr^{-1}; Sulphate 1.3-1.6 keq/ha/yr^{-1}, and 'High' acid load = Nitrate 1.0 keq/ha/yr^{-1}; Sulphate 2.3 keq/ha/yr^{-1}).



The second phase of this exercise involved examining the depletion of the calcium content of rocks in relation to the cumulative amount of acid deposition over time. Data from Warren Springs Laboratory was used to create a historical trend of acid deposition in the MAGIC model (Warren-Spring-Laboratory, 1987). This has been tailored to reflect the patterns of (i) Early industrial growth in the late 1850s; (ii) 'Tall stacks' policies after the

Clean Air Acts in the 1950s and 1960s; (iii) Peak emissions in the late 1970s; and (iv) Emissions curtailment following international agreements in the 1980s and 1990s. The amount of deposition received by the ten study catchments since 1940 was estimated using the 'scale factors' in the MAGIC deposition hindcast sequence (Table 4.13). The 'scale factors' reflect the increases / decreases in deposition in relation to current deposition (which has a scaling factor of 1.0). After this calculation, the calcium compositions of the ten Borrowdale Volcanic rock samples were plotted against the estimated cumulative amount of acid deposition since 1940 (Figure 4.13).

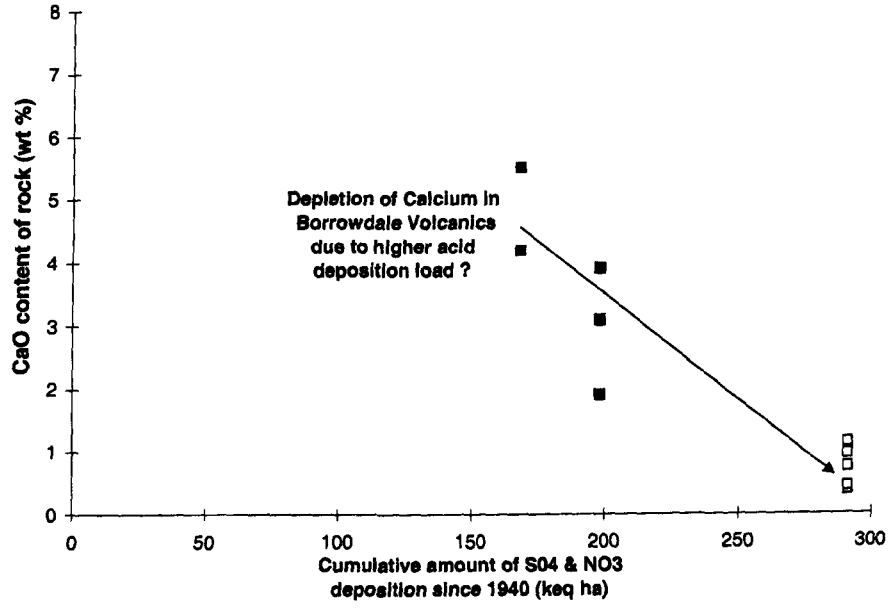
Table 4.13 - Table showing calculation of the cumulative amount of acid deposition received by the ten Borrowdale Volcanic catchments since 1940.

Present Nitrate Dep (keq/ha/yr^{-1})	Present Sulphate Dep (keq/ha/yr^{-1})	Scale Factor	No. of years	Year of Step	Cumulative Deposition
0.6	1.6	1.2	10	1940-50	26.5
		1.8	11	1950-61	69.0
		1.9	6	1961-67	93.7
		1.9	9	1967-76	132.1
		1.8	11	1976-87	175.8
		1.0	10	1987-97	197.8
0.5	1.3	1.2	10	1940-50	22.5
		1.8	11	1950-61	58.5
		1.9	6	1961-67	79.5
		1.9	9	1967-76	112.0
		1.8	11	1976-87	149.1
		1.0	10	1987-97	167.8
1.0	2.3	1.2	10	1940-50	39.0
		1.8	11	1950-61	101.5
		1.9	6	1961-67	137.9
		1.9	9	1967-76	194.3
		1.8	11	1976-87	258.6
		1.0	10	1987-97	291.1

The rock samples exhibit a decline in the calcium content of the rock surface with increasing acid deposition (Figure 4.13). That is, the rocks that received the least amount of cumulative acid deposition since 1940 (167.8 keq/ha of sulphate and nitrate) have the highest surface calcium content (4-5.5 %); the rocks that received the intermediate amount of cumulative acid deposition (197.8 keq/ha of sulphate and nitrate) have an intermediate

surface calcium content (1.75-3.75 %); and the rocks that received the highest amount of cumulative acid deposition (291.1 keq/ha of sulphate and nitrate) have the lowest surface calcium content (< 1 %). This may suggest that acid deposition has accentuated the amount of calcium leaching from the rock's surface. To attribute this to acid rain, however, we would have to assume that all the rocks had similar calcium content in the first place, and this is not known. However, this could possibly be explored further by using borehole data from the British Geological Survey.

Figure 4.13 - Diagram comparing the calcium compositions of 10 Borrowdale Volcanic Group rock samples in relation to the cumulative amount of acid deposition they have received since 1940.



b. Catchment contribution via water-rock interactions and human influences

Streamwater chemical data are bound to be subject to a certain degree of noise. This method tries derive only the components added solely from within the catchment. It is possible to correct streamwater chemistry for the chemical contribution of rainfall and evapotranspiration effects using chloride. This method has been previously used in the hydrochemistry field by UK researchers (For example, Shand *et al.*, 1994; Edmunds and Key, 1996). As with the Cl balance deposition method (Section 4.2.2), chloride in rainfall is assumed to behave conservatively during the recharge process and the following formula was used to remove the rainfall inputs:

$$\text{Catchment Contribution} = X_c - \left[\frac{Cl_w}{Cl_r} * X_r \right]$$

where X_c is the solute concentration of stream sample;
Cl_w is the chloride in the streamwater sample;
Cl_r is the chloride in rainwater; and
X_r is the rainwater solute concentration.

The flow-weighted streamwater chemistry of each of the 55 study sites was corrected for sodium, magnesium, calcium, potassium and sulphate using this method. The ratios were calculated using the catchment contribution data, except Na/Cl which was calculated using the streamwater data. The catchment data was aggregated into the five geological groups previously used and the results are given below (Table 4.14).

Table 4.14 - Catchment contribution of each lithological unit after subtracting rainfall, corrected for evapotranspiration using chloride. (Units: μeq l^{-1})

	Borrowdale Volcanics	Silurian Slates	Skiddaw Slates	Granite	Mixed Lithology
Evaporation factor	1.12	1.70	1.66	1.98	1.05
Sodium	11.06	2.73	6.83	13.35	33.51
Magnesium	23.24	34.96	16.49	20.64	45.40
Calcium	127.80	283.09	79.14	49.60	173.01
Potassium	2.52	0.97	4.39	4.25	0.32
Sulphate	0.62	2.11	1.61	- 36.72	7.42
Chloride	0	0	0	0	0
Na:Cl	0.95	0.83	0.81	0.92	1.17
Na:Ca	0.09	0.01	0.09	0.27	0.19
Mg:Ca	0.18	0.12	0.21	0.42	0.26
K:Na	0.23	0.36	0.64	0.32	0.01

Recalculating the chemical data in this way suggests that some ions have large catchment contributions from water-rock interactions whilst others show smaller contributions from water-rock interactions. For example, calcium and magnesium

contributions from the catchment are large, whilst sodium, potassium and sulphate contributions from the catchment are small. As calcium and magnesium contributions are the largest, they are also presented graphically to ease interpretation (Figure 4.14 and 4.15).

The catchment contribution of calcium is high in the Silurian Slates (283 μeq l^{-1}), moderately high in the Mixed lithology (173 μeq l^{-1}), low in Borrowdale Volcanic (128 μeq l^{-1}), and very low in Granite (50 μeq l^{-1}) and Skiddaw Slate (80 μeq l^{-1}) catchments (Figure 4.14).

Figure 4.14 - Catchment contribution of calcium categorised by rock type. (Units:μeq l^{-1})
Key: BVG – Borrowdale Volcanic Group; SKS – Skiddaw Slates; GR – Granite; SIL– Silurian Slates; MIX – Mixed Lithology

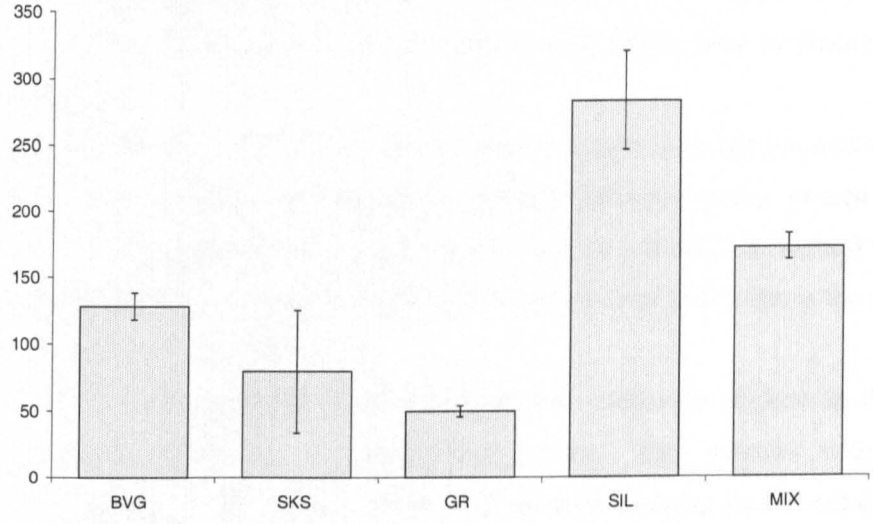
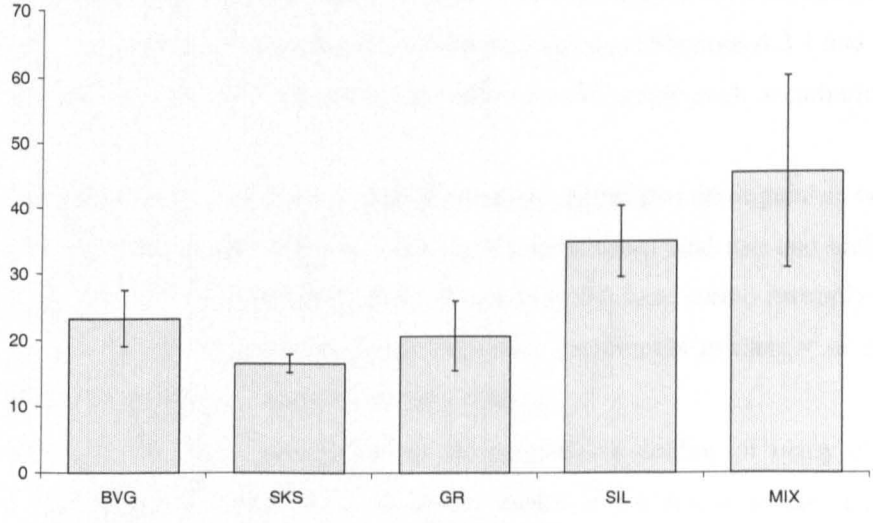


Figure 4.15 - Catchment contribution of magnesium categorised by rock type.
(Units are annual catchment contribution in μeq l^{-1}).
Key: BVG – Borrowdale Volcanic Group; SKS – Skiddaw Slates; GR – Granite; SIL– Silurian Slates; MIX – Mixed Lithology



The catchment contribution of magnesium is fairly high in the Silurian Slates and Mixed lithology (35-45 μeq l^{-1}) and moderate in the Borrowdale Volcanic, Skiddaw Slates and Granite (16-23 μeq l^{-1}) catchments (Figure 4.15).

According to Table 4.14, the catchment contribution of sodium is moderate in the Mixed lithology (33 μeq l^{-1}), low in the Borrowdale Volcanic, Silurian Slates and Granite (7-13 μeq l^{-1}) and very low in Silurian Slate (3 μeq l^{-1}) catchments; for potassium it is low in the Borrowdale Volcanics, Skiddaw Slates and Granite (3-4 μeq l^{-1}) and very low in the Silurian Slates and Mixed lithology (< 1 μeq l^{-1}) catchments; and for sulphate it is low in the Mixed lithology (7 μeq l^{-1}) and very low in the Borrowdale Volcanics, Silurian Slates and Skiddaw Slates (< 2 μeq l^{-1}) catchments. There is net loss of sulphate to the catchment in Granite catchments (-37 μeq l^{-1}). This is possibly the result of some sulphate reduction in the peaty soils.

In addition, the Na/Cl ratio in rain is usually around 0.86 but the mean values for the Borrowdale Volcanics, Granite and the Mixed lithology group exceed this. This suggests that these catchments have a catchment source of sodium. The highest Na/Cl ratio was found in the Mixed lithology group (1.17). A possible reason for this is the presence of carbonate cement in some of the rocks.

In general, the catchment contribution of base cations is highest in the Silurian Slates catchments, suggesting a well-buffered system. This concurs with the high concentrations found in the water chemistry of streams draining this lithological group (Sections 4.3.1 and 4.3.2), and is supported by the large amount of weathering identified in the whole-rock weathering patterns (Section 3.5.3). Conversely, the catchment contribution of base cations is lowest in the Skiddaw Slate and Granite catchments suggesting a 'sensitive' system. This is in agreement with the low chemical concentrations found in the water chemistry of streams draining these lithological groups (Sections 4.3.1 and 4.3.2), and is supported by the lack of weathering identified in the whole-rock weathering patterns (Section 3.5.3).

This method helps to detect a unique chemical signal that distinguishes between the contributions from the catchment (i.e. water-rock interactions, land use and anthropogenic influences) and rainfall. It is a useful aid for interpreting the base cation resupply to discrete catchments and can be used to differentiate between catchments in danger of progressive acidification and catchments which are better buffered.

Given that acid rain has resulted in the progressive decline of many of the UK's aquatic and terrestrial ecosystems, it would be useful if the future stream chemistry of pristine catchments could be predicted accurately. One way of predicting the future is

through modelling, which is discussed in Chapter 5. However, a less data-intensive method is to use space as a surrogate for time. The next section explores the possibilities of such an approach (Section 4.3.4).

4.3.4. Using space as a surrogate for time to assess the effects of land use conversion and/or climate change

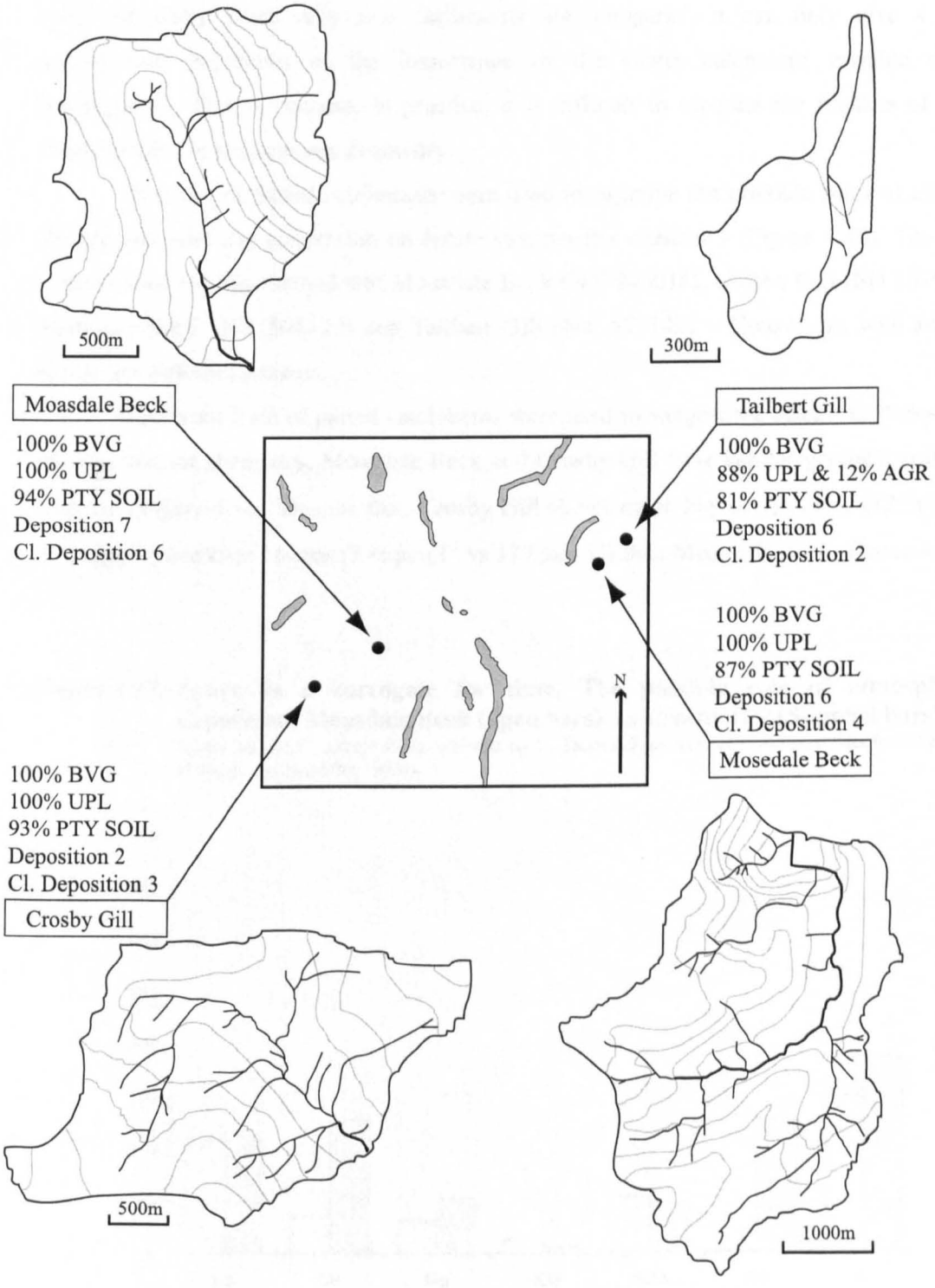
A version of this section has been published in the paper: GJP Thornton & NB Dise (1998). The sensitivity of streams to acid deposition in the English Lake District: the role of catchment characteristics. *Hydrology in a Changing Environment - Volume 1 (Eds. H Wheater & CJ Kirkby), John Wiley & Sons, London, p547-58.*

Concern about acid rain continues to be a relevant issue despite a decline in sulphur emissions since the 1980s (UKRGAR, 1997). While sulphur emissions in the U.K., Europe and North America have been falling due to the implementation of reduction strategies, nitrogen emissions have continued to increase. This has sparked a debate over whether an increase in nitrogen deposition will offset any improvements in streamwater chemistry resulting from the decreased sulphur load (Battarbee, 1997; Murlis, 1997). Estimating critical loads of pollutants (For example, Bull, 1997; Curtis *et al.*, 1997; Kernan *et al.*, 1998) and modelling the rate of recovery of acidified areas (Jenkins and Ferrier, 1997) are also the subjects of major current research.

In addition to the threat of acid rain, the UK is gradually running out of space and resources for its ever increasing population. Amongst others, the Forestry Commission and MAFF are responsible for converting 'unprofitable' pristine areas to 'money-making' coniferous plantations and intensive agricultural land. The conversion of formerly pristine catchments to intensively managed catchments may have a large role to play in the future, and thus may significantly modify the water chemistry of the streams draining the UK.

In order to estimate the effects of land use and climatic change, catchments are selected to compare how stream chemistry might alter under varying future scenarios. The method of estimating streamwater chemistry under different scenarios utilises space as a surrogate for time. Essentially this method entails taking two similar catchments, except for one catchment characteristic (i.e. geology, soil, land use, deposition), and comparing the output chemistry. The difference between the two catchments is over space, however it is possible to suggest that the present situation at one stream might happen to the other stream in the future (i.e. the difference in space is used as a surrogate for the difference over time). Therefore, the 'different' catchment characteristic (be it soil, land use or whatever) is considered responsible for the resulting difference in the 'future' stream chemistry.

Figure 4.16 - Location, catchment diagrams and catchment characteristic information for the sites used in the space as surrogate for time method.

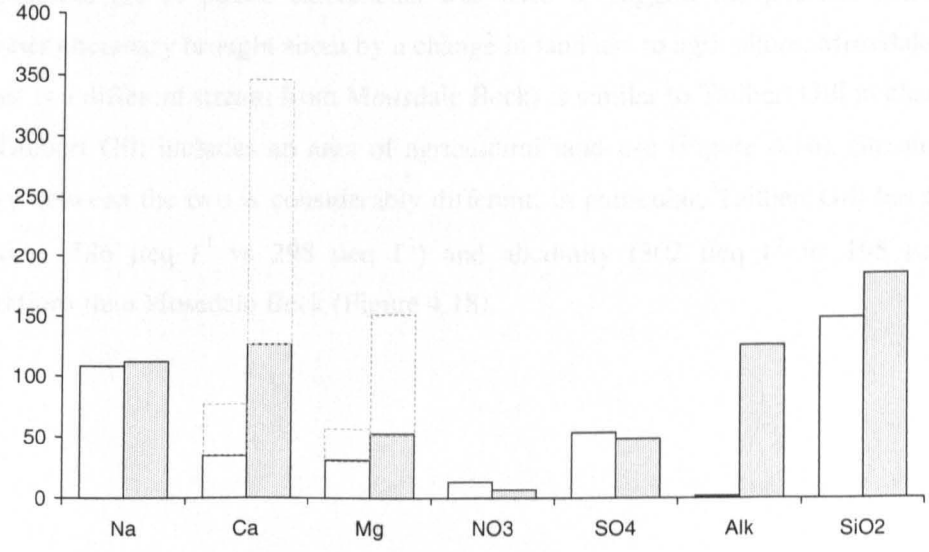


There are a number of inherent problems in comparing streams since no two catchments have identical relief, soils, geology or hydrology (Nisbet, 1990). The 'space as a surrogate for time' technique assumes that there are no other factors influencing water chemistry besides the geology, soil, land use and deposition. Since this is obviously not the case, especially when only two catchments are compared, it can only give a very approximate indication of the importance of the single catchment variable under investigation. This is because, in practice, it is difficult to separate the impacts of each characteristic on streamwater chemistry.

Two sets of paired catchments were used to examine the possible roles of climate change and land use conversion on future streamwater chemistry (Figure 4.16). The four streams used for this method are: M*oas*dale Beck (NY 246018), Crosby Gill (SD 187953), M*ose*dale Beck (NY 504120) and Tailbert Gill (NY 534142) – Note becks with similar names are different streams.

Data from a set of paired catchments were used to suggest the effects of deposition on streamwater chemistry. Moasdale Beck and Crosby Gill have similar geology, soil and land use (Figure 4.16). Despite that, Crosby Gill shows much higher alkalinity (125 $\mu eq\ l^{-1}$ vs 1 $\mu eq\ l^{-1}$) and base cations (298 $\mu eq\ l^{-1}$ vs 177 $\mu eq\ l^{-1}$) than Moasdale Beck (Figure 4.17).

Figure 4.17 - Space as a surrogate for time. The possible role of atmospheric deposition: Moasdale Beck (open bars) Vs Crosby Gill (Stippled bars).
(Units are $\mu eq\ l^{-1}$, except silica, which is $\mu g\ l^{-1}$. Dashed lines represent historical data from 1971-74 (Carrick and Sutcliffe, 1983)).

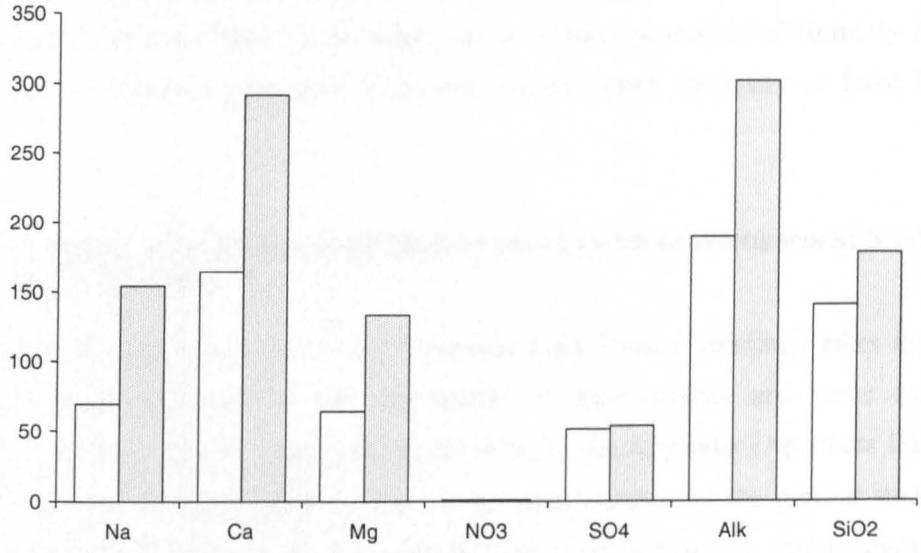


Although at present sulphate levels of the two streams are relatively similar, the nitrate levels at Moasdale Beck are twice that of Crosby Gill. It is therefore possible that the base cation depletion in Moasdale Beck is attributable to an influx of acid anions from the atmospheric deposition load, which is twice that of Crosby Gill (DEP 7 vs DEP 2). However, given the problems of the 20 x 20km atmospheric deposition this seems like it might be an overestimate of the atmospheric deposition difference. Indeed, the Cl balance deposition method suggests that atmospheric deposition at Crosby Gill is actually around 70 % of that experienced by Moasdale Beck.

The timescale for the water quality decline is unknown. However, the two sites have been sampled historically (Carrick and Sutcliffe, 1983), which may give some indication of the timescale for the decline. The base cation concentrations at both sites seem to have become significantly depleted since the early 1970s, especially at Crosby Gill (Figure 4.17). One explanation for this might be the difference in the base cation content of the rocks or soils. Although the geology is similar, we have already seen that the provision of base cations supplied via rock weathering might eventually slow under higher acid deposition loads (Section 4.3.3) and thus the water chemistry will decline rapidly at both sites because there is little to buffer the incoming acid precipitation. However, the reduction in weathering may have occurred at Moasdale Beck first (due to the increased deposition load), which may account for the difference in the streamwater chemistry. However the rapid decline over the past 25 years suggests that Crosby Gill may now be experiencing similar problems to those encountered by Moasdale Beck (i.e. progressive acidification is occurring due to low base cation resupply to the catchment).

Another set of paired catchments was used to suggest the possible effects on streamwater chemistry brought about by a change in land use to agriculture. M*ose*dale Beck (note: this is a different stream from M*oas*dale Beck) is similar to Tailbert Gill in character, except Tailbert Gill includes an area of agricultural land use (Figure 4.16). Streamwater chemistry between the two is considerably different; in particular, Tailbert Gill has higher base cation (586 $\mu eq\ l^{-1}$ vs 298 $\mu eq\ l^{-1}$) and alkalinity (302 $\mu eq\ l^{-1}$ vs 195 $\mu eq\ l^{-1}$) concentrations than Mosedale Beck (Figure 4.18).

Figure 4.18 - Space as a surrogate for time. The possible role of land use: Mosedale Beck (open bars) Vs Tailbert Gill (Stippled bars).
(Units are μeq l^{-1}, except silica, which is μg l^{-1})



In Section 4.3.2, it was noted that catchment modification to agricultural land use seems to add large amounts of alkalinity, base cations and nitrate, approximately doubling alkalinity and tripling nitrate concentrations. It may be that the addition of only 12% agriculture has led to an increase in alkalinity of approximately 100 μeq l^{-1} primarily from the addition of base cations. It is likely that the artificial influx of base cations results from the land improvement and catchment liming (cf. Parry *et al.*, 1982). However, nitrate levels are similar (and low) in both catchments, which may suggest that there is a threshold for nitrogen retention within the catchment, which is yet to be breached. The two sites have not been sampled historically, therefore no strong assessment can be made to decide whether the water chemistry differences are inherent, or actually occurred post-modification.

Although this approach has its weaknesses, it is a fairly simple method of predicting the future water chemistry of streams. Its reliability increases with the number of similar sites being compared. Using this technique, it is possible to make some estimates of how water chemistry might vary in response to a future change in catchment conditions.

The sites in the 'role of atmospheric deposition' exercise (Figure 4.17) may suggest that progressive acidification caused by excessive acid deposition is occurring at these sites. However, it may also be due to many other processes we haven't considered. For the sake of argument, if we assume that progressive acidification **is** occurring, the large chemistry

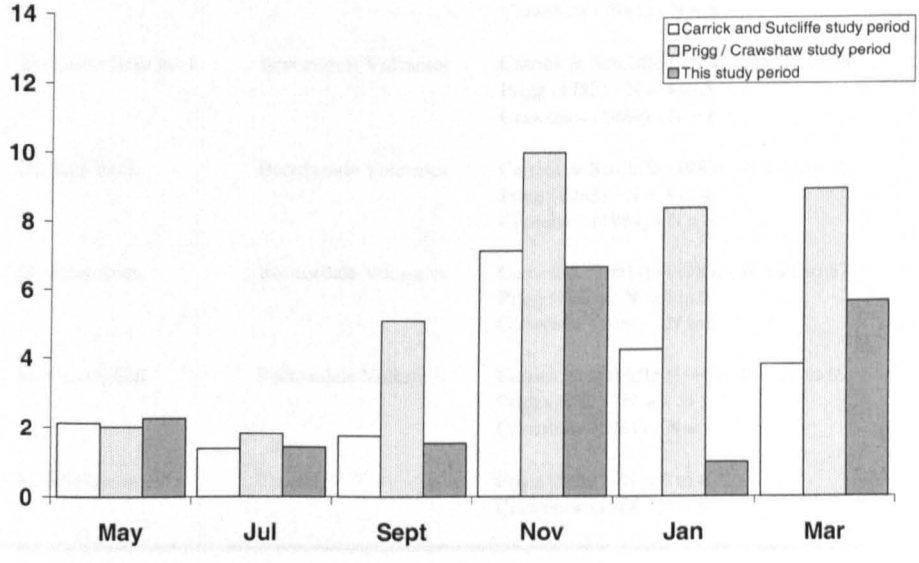
difference is probably caused by the leaching of cations from soil exchange sites outstripping the base cation supply from rocks due to increased acid deposition.

The sites in the 'role of land use' exercise (Figure 4.18) lend support to the findings of the previous sections in this thesis. For example, the segregation of the Silurian Slates in Sections 4.3.1 and 4.3.2 showed the implications of the conversion of formerly pristine catchments to intensively managed catchments on the water chemistry of Lake District streams.

4.4. Comparing the present Lake District results with previous work: Study results in context

Several studies have previously examined Lake District streams / lakes and their associated water chemistry. A full description of these studies and some exercises comparing historical stream / tarn data can be found in the Appendix (Appendix D). Some of the 'historical' studies sampled a few of the same streams as the present study. The streamwater data from these sites are compared with the data from the current study to put the present work in context and assess the water chemistry trends over time. However, in order to make scientifically robust comparisons the flow from each survey must be taken into account. The mean flow from each survey period is compared to the present study in Figure 4.19.

Figure 4.19 - Mean monthly flow from 8 gauged sites for 1970-75 (open bars) and 1982-83 (stippled bars) compared with mean monthly flow for the survey period, 1996-97 (filled bars). (Units are $m^3 sec^{-1}$)



The mean monthly flow during the Carrick and Sutcliffe study (1970-75) and present study (1996-97) are fairly similar (Figure 4.19) suggesting that comparisons can be made between the two studies with a degree of confidence. In contrast, flow during the Prigg / Crawshaw studies (1982-83) are always higher than the present study and thus comparisons can be made with less certainty.

4.4.1 Mean data from the current and historical studies

There were eleven sites sampled by the current study that had been previously sampled (Table 4.15). The mean data of the individual sites sampled by the previous studies were compared with the mean data from the current study to determine whether any change in water chemistry had taken place during the intervening period (Table 4.16).

Table 4.15 - Table showing the eleven current sample sites that have been previously sampled and are reported in the following publications herein.

Stream & Site No.	Geology	Study & No. of samples
1. Rydal Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 6
2. Stock Ghyll	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 14
11. Stony Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 5
13. Trout Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 5
14. Woundale Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 33
26. Moasdale Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 33 to 94 Prigg (1983) - N = 4 to 5 Crawshaw (1984) - N = 8
27. Castle How Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 23 to 38 Prigg (1983) - N = 4 to 5 Crawshaw (1984) - N = 8
28. Tarn Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 18 to 68 Prigg (1983) - N = 3 to 4 Crawshaw (1984) - N = 8
29. Sling Beck	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 28 to 87 Prigg (1983) - N = 4 to 5 Crawshaw (1984) - N = 8
31. Crosby Gill	Borrowdale Volcanics	Carrick & Sutcliffe (1983) - N = 29 to 89 Prigg (1983) - N = 4 to 5 Crawshaw (1984) - N = 8
34. Whillan Beck	Granite	Prigg (1983) - N = 7 to 8 Crawshaw (1984 - N = 8

Table 4.16 - Table showing the water chemistry data from the previous studies in context with the data from the current study for the eleven stream sites.
(Units are μeq l^{-1}, except pH. Figures in parentheses are ± 1 S.E., except Prigg (1983) and Crawshaw (1984) studies which are the data range).

Stream	Na	Mg	Ca	pH	Cl	Study & No. of samples
1. Rydal Beck	163.5 (4.8)	88.7 (8.7)	229.2 (18.1)	6.9 (0.05)	180.2 (6.4)	Carrick & Sutcliffe (1983) - N = 6
	105.7 (7.7)	56.5 (4.3)	150.7 (9.5)	6.9 (0.12)	121.9 (6.1)	This Study - N = 6
2. Stock Ghyll	329.6 (19.6)	117.5 (9.6)	408.6 (23.3)	7.2 (0.07)	345.4 (22.7)	Carrick & Sutcliffe (1983) - N = 14
	196.5 (11.7)	66.9 (9.0)	233.2 (15.1)	7.1 (0.20)	264.8 (20.3)	This Study - N = 6
11. Stony Beck	193.2 (7.1)	87.2 (11.7)	205.0 (17.9)	7.0 (0.06)	213.0 (9.5)	Carrick & Sutcliffe (1983) - N = 5
	91.8 (12.7)	56.7 (11.8)	111.4 (21.9)	7.0 (0.22)	78.0 (6.7)	This Study - N = 6
13. Trout Beck	192.0 (7.3)	80.8 (9.9)	279.0 (28.0)	6.8 (0.07)	209.0 (9.6)	Carrick & Sutcliffe (1983) - N = 5
	86.2 (10.8)	36.3 (6.8)	142.5 (27.6)	6.9 (0.16)	79.6 (8.6)	This Study - N = 6
14. Woundale Beck	223.4 (8.1)	132.8 (8.1)	306.1 (16.8)	7.1 (0.06)	220.6 (9.3)	Carrick & Sutcliffe (1983) - N = 33
	108.4 (11.3)	53.0 (10.2)	129.8 (22.2)	7.0 (0.18)	109.4 (12.3)	This Study - N = 6
26. Moasdale Beck	137.9 (1.7)	43.0 (2.4)	55.9 (1.3)	5.1 (0.03)	-	Carrick & Sutcliffe (1983) - N = 33 to 94
	-	-	60 (*50-75*)	4.8 (*4.5-5.3*)	-	Prigg (1983) - N = 4 to 5
	-	-	69 (*50-160*)	4.9 (*4.5-5.3*)	-	Crawshaw (1984) - N = 8
	108.2 (6.8)	31.1 (2.6)	36.5 (5.8)	5.7 (0.14)	-	This Study - N = 6
27. Castle How Beck	172.2 (3.8)	65.9 (3.4)	123.8 (5.4)	5.7 (0.11)	-	Carrick & Sutcliffe (1983) - N = 23 to 38
	-	-	135 (*95-205*)	5.0 (*4.7-6.5*)	-	Prigg (1983) - N = 4 to 5
	-	-	96 (*50-125*)	5.0 (*4.5-6.5*)	-	Crawshaw (1984) - N = 8
	171.0 (18.4)	62.2 (2.6)	124.4 (18.2)	6.3 (0.07)	-	This Study - N = 6
28. Tarn Beck	154.2 (2.2)	72.2 (3.3)	111.2 (2.3)	5.9 (0.04)	-	Carrick & Sutcliffe (1983) - N = 18 to 68
	-	-	115 (*90-160*)	6.5 (*6.2-7.0*)	-	Prigg (1983) - N = 3 to 4
	-	-	107 (*80-160*)	6.6 (*5.9-8.2*)	-	Crawshaw (1984) - N = 8
	115.7 (8.8)	50.6 (4.5)	82.6 (8.5)	6.6 (0.14)	-	This Study - N = 6
29. Sling Beck	189.9 (3.2)	106.3 (4.5)	144.7 (3.6)	6.4 (0.05)	-	Carrick & Sutcliffe (1983) - N = 28 to 87
	-	-	150 (*65-265*)	6.6 (*6.1-7.0*)	-	Prigg (1983) - N = 4 to 5
	-	-	151 (*75-265*)	6.4 (*5.7-7.0*)	-	Crawshaw (1984) - N = 8
	96.0 (6.7)	48.9 (7.9)	69.6 (11.9)	6.7 (0.19)	-	This Study - N = 6
31. Crosby Gill	234.8 (3.5)	157.0 (11.3)	339.6 (12.7)	6.5 (0.05)	-	Carrick & Sutcliffe (1983) - N = 29 to 89
	-	-	404 (*260-494*)	6.9 (*6.3-7.7*)	-	Prigg (1983) - N = 4 to 5
	-	-	363 (*190-599*)	7.0 (*6.3-7.7*)	-	Crawshaw (1984) - N = 8
	112.4 (8.4)	60.0 (10.0)	135.6 (18.3)	7.1 (0.13)	-	This Study - N = 6
34. Whillan Beck	-	-	145 (*80-190*)	5.9 (*5.1-7.2*)	-	Prigg (1983) - N = 7 to 8
	-	-	118 (*55-190*)	6.1 (*5.0-7.2*)	-	Crawshaw (1984 - N = 8
	-	-	92.2 (7.4)	6.6 (0.16)	-	This Study - N = 6

Sodium concentrations are always lower in the present study than in the Carrick and Sutcliffe (1983) study. The sodium concentration in Carrick and Sutcliffe (1983) study ranges between 137.9 μeq l^{-1} (Moasdale Beck) and 329.6 μeq l^{-1} (Stock Ghyll), whereas in the present study it ranges between 86.2 μeq l^{-1} (Trout Beck) and 196.5 μeq l^{-1} (Stock Ghyll).

Magnesium concentrations are always lower in the present study than in the Carrick and Sutcliffe (1983) study. The magnesium concentration in Carrick and Sutcliffe (1983) study ranges between 43.0 μeq l^{-1} (Moasdale Beck) and 157.0 μeq l^{-1} (Crosby Gill), whereas in the present study it ranges between 31.1 μeq l^{-1} (Moasdale Beck) and 66.9 μeq l^{-1} (Stock Ghyll).

Calcium concentrations are almost always lower in the present study than in the Carrick and Sutcliffe (1983) study, the exception is Castle How Beck which has very similar concentrations in both studies. On the whole, calcium concentrations in the Prigg (1983) and Crawshaw (1984) studies are similar to those found in the Carrick and Sutcliffe (1983) study. The calcium concentration in Carrick and Sutcliffe (1983) study ranges between 55.9 μeq l^{-1} (Moasdale Beck) and 408.6 μeq l^{-1} (Stock Ghyll), whereas in the present study it ranges between 36.5 μeq l^{-1} (Moasdale Beck) and 233.2 μeq l^{-1} (Stock Ghyll).

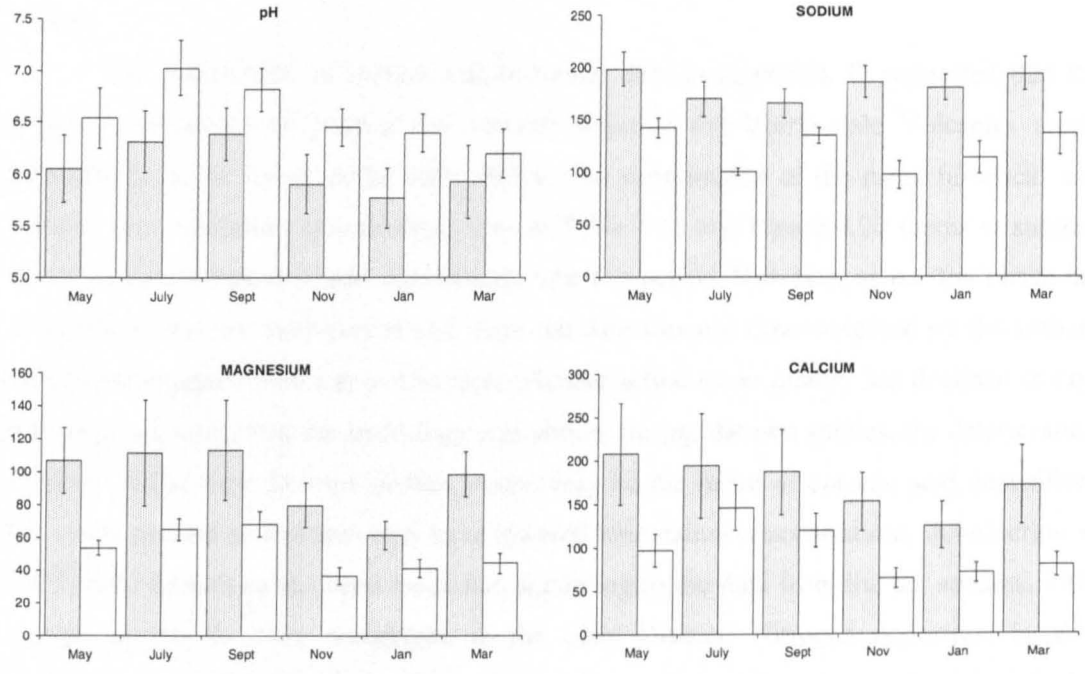
Chloride concentrations are always lower in the present study than in the Carrick and Sutcliffe (1983) study. The chloride concentration in Carrick and Sutcliffe (1983) study ranges between 180.2 μeq l^{-1} (Rydal Beck) and 345.4 μeq l^{-1} (Stock Ghyll), whereas in the present study it ranges between 78.0 μeq l^{-1} (Stony Beck) and 264.8 μeq l^{-1} (Stock Ghyll).

pH is generally higher in the present study than in the Carrick and Sutcliffe (1983) study. pH in Carrick and Sutcliffe (1983) study ranges between pH 5.1 (Moasdale Beck) and pH 7.2 (Stock Ghyll), whereas in the present study it ranges between pH 5.7 (Moasdale Beck) and pH 7.1 (Stock Ghyll and Crosby Gill). However, the pH values in the present study may be high due to problems with carbon dioxide degassing during analysis (Full details in Section 2.4.1a).

4.4.2 Mean monthly data from the current and historical studies

Of the comparison studies, only the Carrick and Sutcliffe (1983) study possessed individual data for each month (Prigg and Crawshaw studies gave the annual mean and the range only). Therefore, only the Carrick and Sutcliffe (1983) study was used in this section for comparison purposes thus reducing the number of sites to ten. The monthly data in the present study is based on a single spot sample at each site, whereas the data from Carrick and Sutcliffe (1983) is an average value for the month calculated from weekly measurements over a longer survey period (n = 18 to 94 samples). The change over time is assessed by looking at the mean monthly averages from the ten streams sampled by both studies in Figure 4.20.

Figure 4.20 - Current mean concentrations of the ten sampling sites (open bars) compared with the mean historical data for the same sampling months as reported by Carrick and Sutcliffe, 1983 (stippled bars).
(Units are μeq l^{-1}. Error bars are ± 1 S.E.)



Mean pH exhibits very similar patterns between the two studies and is always higher in the present study (upto 0.5 pH units). pH in the Carrick and Sutcliffe (1983) study ranges between pH 5.75 (January) and pH 6.4 (September), whereas in the present study it ranges between pH 6.25 (March) and pH 7.0 (July). However, as mentioned beforehand, the pH values in the present study may be high due to problems with carbon dioxide degassing during analysis.

Mean sodium concentrations exhibit very similar patterns between the two studies and are always lower in the present study (upto 75 μeq l^{-1}). The sodium concentrations in the Carrick and Sutcliffe (1983) study ranges between 160 μeq l^{-1} (September) and 200 μeq l^{-1} (May), whereas in the present study it ranges between 100 μeq l^{-1} (July / November) and 140 μeq l^{-1} (May).

Mean magnesium concentrations exhibit similar patterns between the two studies and are always lower in the present study (upto 60 μeq l^{-1}). The magnesium concentrations in the Carrick and Sutcliffe (1983) study ranges between 60 μeq l^{-1} (January) and 110 μeq l^{-1} (July / September), whereas in the present study it ranges between 40 μeq l^{-1} (November) and 70 μeq l^{-1} (September).

Mean calcium concentrations are always lower in the present study (upto 100 μeq l^{-1}) and exhibit very similar monthly patterns in both studies. The calcium concentrations in the Carrick and Sutcliffe (1983) study ranges between 125 μeq l^{-1} (January) and 200 μeq l^{-1} (May), whereas in the present study it ranges between 50 μeq l^{-1} (November) and 140 μeq l^{-1} (July).

The comparison of current and historical data in Appendix D suggested that the ionic concentrations of present day streams draining the Borrowdale Volcanics aren't dissimilar to those found in the early 1970s. The examination of the mean historical and current water chemistry of individual sites in Table 4.16 and Figure 4.20 seems to suggest that water quality has declined significantly over this period. However, as we don't have the actual daily flow for each period and since the data was not flow-weighted by the authors we can not suggest (with any confidence) whether actual water quality has declined or not. However, assuming that the hydrology was similar during the two studies, the deterioration of many of the Lake District surface waters may be the result of chronic acid deposition. The stress exerted on this area may have lowered base cation concentrations. A reduction in UK sulphur emissions has been made but, according to the data from the ten streams, little change has so far been recognised in the Lake District. Nitrogen deposition is also becoming increasingly important so the added influx of nitrogen may be causing the amelioration resulting from the reduction in sulphur emissions to be offset.

4.5. Summary of Chapter

During this chapter, the water data from the stream catchments were examined in relation to the catchment characteristics. The primary aim of this chapter was discuss the sensitivity to acidification of Lake District streams and make some inferences about the relative roles of the catchment characteristics in determining streamwater chemistry.

Using the 200 μeq l^{-1} threshold for sensitivity to acidification (Section 1.1.2), fifty-one streams (93%) recorded calcium concentrations below the threshold at least once during the six surveys, with nineteen of the streams (35%) recording calcium concentrations below this level throughout the entire study period. In addition, fifty-four streams (98%) recorded alkalinities below the threshold at least once during the six surveys, with twenty-one of the streams (38 %) recording alkalinities below 50 μeq l^{-1} on at least one occasion. Furthermore, nine streams (16 %) had nitrate concentrations in excess of 50 μeq l^{-1} at least once during the six surveys, with four streams consistently above the 50 μeq l^{-1} level.

Alkalinity (2 to 452 μeq l^{-1}) and calcium (24 to 656 μeq l^{-1}) exhibited a large range

in the mean annual flow-weighted data. Forty-one (75%) of the streams can be considered sensitive to acidification on the basis of their alkalinity and thirty-eight (69%) can be considered sensitive to acidification on the basis of their calcium concentrations.

Borrowdale Volcanic, Skiddaw Slate, Granite, Upland, THI soil and PTY soil catchments have low base cation and alkalinity concentrations, whereas Silurian Slate, mixed lithology, agricultural, THP soil and GLY soil catchments have the high base cation and alkalinity concentrations. Nitrate concentrations were generally low (< 20 $\mu eq\ l^{-1}$) with the exception of agriculture and THP soil catchments which have high nitrate concentrations (80-120 $\mu eq\ l^{-1}$).

Four catchments were examined using the 'space as a surrogate for time' technique to make some estimates of how water chemistry might vary in response to a future change in catchment conditions. Acid deposition may have had major implications for the chemistry of streams in the Lake District as the difference between the alkalinities at the two 'deposition' sites was very large. The conversion of pristine catchments to agriculture also may have major ramifications for the chemistry of streams in the Lake District as there is a significant decline in water quality between the two 'land use' sites.

The comparison with the historical data suggests that Lake District water quality has declined significantly between the early 1970s and present day. This deterioration may be the result of chronic acid deposition and a reduction in catchment buffering. UK sulphur emissions have been reduced but streamwater chemistry may take a long time to return to 1970 levels. With the increasing importance of nitrogen deposition, it may be possible that the reduction in sulphur emissions is being offset.

In summary, the patterns between streamwater chemistry and catchment characteristics reported in this chapter should provide excellent information for interpreting the variables selected in the modelling section (Chapter 5).

CHAPTER 5

Modelling the major-ion chemistry of Lake District streams

"Statistics are like lamp-posts. They should be used for support rather than to light" – Anon

5.1 Introduction

The aim of this chapter is to create a water quality model with the geochemical data from the study catchments, and this process can be separated into four sections: (a) Empirical modelling (Section 5.2); (b) Process-based modelling (Section 5.3); (c) Integrating field data and models (Section 5.4); and (d) Predictive model with special emphasis on acid sensitivity (Section 5.5).

The empirical modelling section begins with a general introduction discussing the purposes/uses and advantages/disadvantages of empirical models (Section 5.2.1), and then assesses the statistical relationships between the geochemical data and catchment characteristics using multiple regression modelling (Section 5.2.2) and principal components analysis (Section 5.2.3). In addition, predictive models for alkalinity were created using the statistical knowledge gleaned from the multiple regression and principal component exercises.

The process-based modelling section begins with a brief introduction discussing the purposes/uses and advantages/disadvantages of process-based models (Section 5.3.1), and then concentrates on a detailed application of MAGIC (Model of Acidification of Groundwater In Catchments) on the study catchments (Section 5.3.2).

In Section 5.4, the possibility that rock chemistry is linked in a predictable way to streamwater chemistry is assessed in two phases: (i) Links between modelled weathering rates and rock weathering patterns (Section 5.4.1); and (ii) Links between rock weathering patterns and surfacewater chemistry (Section 5.4.2)

In the final section, a simple regional predictive model is developed using the knowledge gained during the empirical, process-based and integrated modelling sections. This process can be segregated into 3 sections: (a) Potential 'ingredients' for the new model (Section 5.5.1); (b) Developing and testing the new model on spatial and temporal scales (Section 5.5.2); and (c) Implications of results for the hydrochemical modelling community (Section 5.5.3).

5.2 Empirical Modelling

A variety of empirical models have been developed and applied in investigations of surface water quality, some of which were discussed in Section 1.3.2. In this section, the purposes/uses and advantages/disadvantages of empirical models are briefly discussed to give a background to the modelling undertaken during the study (Section 5.2.1). The main objectives of Section 5.2 are to establish statistical relationships between the geochemical data and the catchment characteristics – this is achieved using multiple regression (Section 5.2.2) and principal components analysis (Section 5.2.3) – and to gain insight about the processes controlling streamwater chemistry. The section concentrates on alkalinity, but some discussion is made about the processes controlling (and the models produced for) key elements like calcium, pH and nitrate. A predictive model of alkalinity in Lake District streams is produced using both the multiple regression and principal components approaches.

5.2.1. Purpose/uses and advantages/disadvantages of empirical models

All models are aggregated representations of reality and many processes and interactions within the system are substituted by a few mathematical equations. There are several main differences between an empirical and a process-based model. An empirical model is developed from observations or experiments and is usually based on the statistical relationship between independent and dependent variables that can be applied even with a very limited amount of information. Its roots in statistics means that the model often indicates relationships without giving any reasons as to how or why those relationships may have occurred. This is an important weakness of empirical models as they use proxy measurements as substitutes for real processes. In contrast, process-based models are based on an understanding of the processes controlling the variables rather than just linking proxy factors to the variables. This is an advantage of process-based models over empirical models, but a fundamental drawback is the large amount of data required to drive a process-based model.

A pre-requisite of using the empirical approach is a sufficient number of observations to establish a significant relationship. Although it can be applied with a very limited amount of information, often stronger statistical relationships result when more observations are available. Although empirical models are usually models based strictly on a statistical relationship, they can also include simple conceptual models that attempt to

incorporate a limited amount of physical reality (Eshleman *et al.*, 1992). Within the surface water quality field, there are five main types of empirical model that have been widely utilised: (i) mass-balance models, (ii) ion-balance (or titration) models, (iii) mixing models, (iv) time-series models, and (v) multiple linear regression models. These models were discussed in Section 1.3.2.

5.2.2. Relationships between water chemistry and catchment characteristics using multiple regression modelling

The examination of streamwater chemistry in Chapter 4 indicated that there are some strong relationships between the chemical constituents and catchment characteristics (Section 4.3). However, the geochemical data were only related in a purely qualitative way to the catchment characteristic categories. Here, multiple linear regression is used to measure the strength of the relationships between streamwater chemistry and catchment characteristics in a quantitative (i.e. statistical) way.

Regression models based on regional or catchment data are an important method of empirical modelling. The conceptual basis behind regression analysis is fully described in Section 2.5.1a, where it is shown that multiple regression analysis evaluates the strength and direction of the relationships between several independent variables (e.g. catchment characteristics) and one dependent variable (e.g. chemical constituent). As with other empirical models, multiple regression models do not establish cause and effect. In some cases variables strongly associated with each other may both be controlled by a third factor.

The straightforward methodology and the low data requirements are the main advantages of regression models. However, an inherent problem with regression (and all other empirical) models is the extrapolation to new cases either in time or space. The fact that causality is not established means that application to conditions other than those from which the model was developed must be made with caution. Therefore, perhaps the major role of empirical models such as multiple regression is to highlight significant relationships between variables, thus allowing hypotheses about the controlling factors to be generated.

During the statistical work, several statistical models with many different independent variable combinations were generated and tested prior to unearthing the 'best' models. Only a brief discussion takes place of the winnowing process that occurred from the 'secondary' statistical models to the 'best' models in this section (the 'secondary' models are given a full statistical discussion in Appendix H).

a. Catchment variables considered in the multiple regression models

This sub-section provides a brief description of the 18 independent variables and also describes the different variable combinations used in each of the four multiple regression models.

Description of the 18 independent variables

The independent variables are split into five groups: geology (5 variables), land use (3 variables), soil (4 variables), deposition (1 variable) and simple site attributes (5 variables). The geology variables are percentage of the catchment underlain by: Borrowdale Volcanics (BVG), Silurian Slates (SIL), Skiddaw Slates (SKS), Granite (GR) and mixed lithology (MIX). The land use variables are percentage of the catchment that is: upland land (UPL), forested land (FOR) and agricultural land (AGR). The soil variables are percentage of the catchment containing: thick, porous soil (THP), thin, impermeable soil (THI), gleyed soil (GLY) and peaty soil (PTY). The geology, land use and soil variables are previously described in Section 4.2.2. The deposition variable is S&N deposition. The seven '20 x 20km grid' deposition load categories were replaced because they don't reflect the effect of deposition alone (Appendix H). The S&N deposition category uses a discrete value for each stream's atmospheric deposition load of sulphur and nitrogen (calculated on a catchment-to-catchment basis using the Cl-balance method – Section 4.2.2) as opposed to the percentage areal coverage. The simple site attribute variables are annual rainfall, annual runoff, site altitude, maximum altitude and distance to the sea.

Different variable combinations utilised by the multiple regression models

The multiple regression models use the flow-weighted data from 44 sites. The 11 sites with significant agricultural land use (> 20%) in the catchment were removed from the analysis because agriculture exerts a large influence on some chemical constituents (e.g. nitrate, calcium) downstream (Section 4.3 and Appendix H). Four different combinations of independent variables were considered in the regression models: (a) All variables together; (b) Geology only; (c) Geology and Deposition; and (d) Geology and simple site attributes (Table 5.1).

Table 5.1 – Catchment variables used in the stepwise regression models.
(excluding agriculture sites – N=44)

Catchment variables	All variables	Geology only	Geology & Deposition	Geology & simple site attributes
BVG	√	√	√	√
SIL	√	√	√	√
SKS	√	√	√	√
GR	√	√	√	√
MIX	√	√	√	√
UPL	√			
FOR	√			
AGR	√			
THP	√			
THI	√			
GLY	√			
PTY	√			
S&N dep	√		√	
Ann Rainfall	√			√
Ann Runoff	√			√
Site altitude	√			√
Max altitude	√			√
Dist to sea	√			√

Multiple regression models of variables significantly correlated to the important chemical constituents of alkalinity (Section 5.2.2b), calcium, pH and nitrate (Section 5.2.2d) are discussed here.

b. Insights into the controlling factors of streamwater alkalinity gained from stepwise multiple regression results

Alkalinity is the key chemical determinand for assessing a stream's acid sensitivity (Altschuller and McBean, 1979; Hendrey *et al.*, 1980; Linthurst, 1983). By using the catchment variables in a stepwise multiple regression, this sub-section attempts to gain some insight into the factors controlling alkalinity. The stepwise method selects particular independent variables based on correlations to the dependent variable. It cannot establish cause and effect but only the presence of a strong statistical association between variables. However, some inferences are attempted as to why the selected variables were selected.

Model including all variables

The stepwise regression method suggested four statistically significant independent variables for alkalinity that account for the highest amount of variation in the flow-weighted concentrations (Table 5.2). We can account for approximately 69% of the variation in the

streamwater concentrations of alkalinity (R^2 of 0.689) by using only four independent variables (S&N deposition, distance to sea, maximum altitude and THP) in the regression model.

Table 5.2 – Stepwise regression model for flow-weighted alkalinity using all independent variables.

Predictive Equation

FW Alk = 233.3 – 56 (S&N Deposition) + 3.03 (Distance to sea) – 0.09 (Max Altitude) – 1.12 (THP)

Regression diagnostics

Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Intercept	233.30	-		-
S&N Deposition (keq ha^{-1} yr^{-1})	-56.00	0.002		39.77
Distance to Sea (km)	3.03	< 0.001	**68.95**	21.76
Maximum Altitude (m)	-0.09	0.033		4.06
THP (% of catchment)	-1.12	0.047		3.36

Parameter Estimate: The parameter estimates are used to parameterise the fitted model. The Intercept provides a value for β_0. This represents the base content, which is an estimate of the value of the response variable if all explanatory variables equalled zero. The estimate for each of the predictors provides values for β_1, β_2 etc.

P value: The P value is an indication of the statistical significance of the explanatory variables in the model. Only variables with a p-value of < 0.05 are selected by the stepwise procedure.

R^2: R^2 is an indication of the proportion of the corrected total variation in the response data that is attributable to the fitted model.

Examining the p-values and the percentage explanation of each variable highlights some of the important factors in controlling streamwater alkalinity. The full model (Table 5.2) suggests that the most highly correlated variables to alkalinity are S&N deposition, which accounts for approximately 40% of the variation (p-value of 0.002), and distance to sea, which accounts for approximately 22% of the additional variation (p-value of < 0.001). Maximum altitude (p-value of 0.033) and THP (p-value of 0.047) are less highly correlated with the stream's alkalinity when the other 2 variables are in the model, they account for only 4% and 3% of the additional variation respectively.

When the direction of the coefficients (Table 5.2) is used to infer the difference between low and high alkalinity sites, a fairly sensible pattern emerges. This approach suggests that sites receiving low S&N deposition and located relatively far from the sea, with low maximum altitudes have high alkalinity. Or alternatively, sites with high

maximum altitude and S&N deposition and located close to the sea have low alkalinity. The final variable, THP (Thick, porous soil), accounts for only 3% of the additional variation in the model and is the only variable that does not afford a ready explanation since it is negatively correlated to alkalinity in the model. When no other variables are considered, alkalinity is high in sites with THP soil (Section 4.3.2b), therefore it is likely that this is a statistical artefact.

The difference in catchment characteristics for high-alkalinity and low-alkalinity sites can be inferred with more confidence if we use our knowledge of the study sites in conjunction with the statistical results. It seems that the stepwise method has differentiated between the sites on the basis of their geographic situation (i.e. lowlands/uplands and maritime/inland). The first three variables selected by the stepwise method provide a strong statistical explanation (R^2 of 0.656), but they also represent a tangible explanation in terms of actual processes. For example, most rainfall is deposited on the sites nearest to the sea and at high altitudes because of orographic uplift. Therefore, sites in this area possess the lowest stream water alkalinity because they receive the highest S&N deposition (due to sea-salt influences and the amount of precipitation). Although the stepwise method didn't select them as statistically significant variables, these sites often have leached, thin soil and resistant bedrock which, associated with the high S&N deposition, exacerbates the problem.

Previous studies have suggested that one of the major factors associated with streamwater alkalinity is the catchment surficial geology (For example, Webb, 1984; Lynch and Dise, 1985; Bricker and Rice, 1989). Geology may well be an important factor in determining the alkalinity of Lake District streams, but the stepwise regression may have identified other factors besides geology because the Borrowdale Volcanic Group, which is chemically and physically heterogeneous (cf. Chapter 3), makes up the majority of the study sites.

Model including geology variables only

The stepwise regression method selected one statistically significant independent variable (SIL), which accounts for approximately 9% (i.e. R^2 of 0.093) of the variation in the streamwater concentrations of alkalinity (Table 5.3).

Table 5.3 – Stepwise regression model for flow-weighted alkalinity using geology variables only.

Predictive Equation

FW Alk = 98.26 + 0.67 (SIL)

Regression diagnostics

Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Intercept	98.26	-		-
SIL (% of catchment)	0.67	0.044	**9.29**	9.29

The 'geology only' model (Table 5.3) suggests that SIL is the most highly correlated with alkalinity – accounting for approximately 9% of the variation (p-value of 0.044). The direction of the coefficient suggests that sites underlain by Silurian Slates have relatively high alkalinity concentrations, whereas sites underlain by other bedrock types have lower alkalinity concentrations. Although the Silurian Slates provide a fairly weak statistical explanation (R^2 of 0.093), they still represent an understandable explanation in terms of the actual processes. It is clear from the geochemical data that alkalinity concentrations are highest in sites underlain by Silurian Slates and the model implies this. According to the geochemical data, Skiddaw Slates and Granite have the lowest alkalinity concentrations but the model does not distinguish them from the Borrowdale Volcanic Group. This is probably due to the fact that the Borrowdale Volcanic Group is so heterogeneous and makes up the majority of the study sites.

Model including geology and deposition variables

When considering geology together with deposition, the stepwise regression method selected two statistically significant independent variables that account for the highest amount of variation in the flow-weighted concentrations of alkalinity (Table 5.4). Approximately 47% of the variation in the streamwater concentrations of alkalinity (R^2 of 0.469) are accounted for by two independent variables (S&N deposition and SKS).

Table 5.4 – Stepwise regression model for flow-weighted alkalinity using geology and deposition variables.

Predictive Equation

FW Alk = 338.8 – 88 (S&N deposition) – 0.73 (SKS)

Regression diagnostics

Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Intercept	338.80	-		-
S&N Deposition (keq ha^{-1} yr^{-1})	-88.00	< 0.001	**46.89**	39.77
SKS (% of catchment)	-0.73	0.024		7.12

The 'geology and deposition' model (Table 5.4) suggests that the most highly correlated variables are S&N deposition, which accounts for approximately 40% of the variation (p-value of < 0.001), and SKS, which accounts for approximately 7% of the additional variation (p-value of 0.024). The direction of the coefficients infer that sites receiving high S&N deposition and underlain by Skiddaw Slates have low alkalinity concentrations, whereas sites underlain by other bedrock types and receiving low S&N deposition have higher alkalinity concentrations.

The variables selected by the stepwise method provide a fairly strong statistical explanation (R^2 of 0.469) and also represent a plausible explanation in terms of actual processes. Since Skiddaw Slates are resistant, base-poor bedrock, the statistical results suggest that sites with low streamwater alkalinity receive high amounts of S&N deposition and are underlain by poorly weathering bedrock.

Model including geology variables and simple site attributes

Since S&N deposition requires fairly detailed data, a regression model using geology and easy-to-measure site attributes was created with a view of potential extrapolation to sites with little detailed information on their chemistry or deposition. The stepwise regression method using these simple site attributes selected three statistically significant independent variables that account for the highest amount of variation in the flow-weighted concentrations of alkalinity (Table 5.5). Approximately 67% of the variation in the streamwater concentrations of alkalinity (i.e. R^2 of 0.673) are accounted for by three independent variables (distance to sea, annual runoff and maximum altitude).

Table 5.5 – Stepwise regression model for flow-weighted alkalinity using geology and simple site attribute variables.

Predictive Equation

FW Alk = 166.18 + 3.38 (Distance to sea) – 0.05 (Annual runoff) – 0.09 (Max Altitude)

Regression diagnostics

Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Intercept	166.18	-		-
Distance to Sea (km)	3.38	< 0.001		36.67
Annual runoff (m^{-3} yr^{-1})	-0.05	0.003	**67.27**	26.22
Maximum Altitude (m)	-0.09	0.026		4.38

The 'geology and simple site attribute' model (Table 5.5) suggests that the most highly correlated variables are distance to sea, which accounts for approximately 37% of the variation (p-value of < 0.001), and annual runoff, which accounts for approximately 26% of the additional variation (p-value of 0.003). Maximum altitude (p-value of 0.009) is less highly correlated with the stream's alkalinity when the other 2 variables are in the model, it accounts for only 4% of the additional variation in the model's final R^2.

Using the direction of the coefficients (Table 5.5) to infer the difference between low and high alkalinity sites results in a reasonably sensible pattern. This approach suggests that sites located large distances from the sea (positive coefficient), with low runoff and relatively low altitude have high alkalinity concentrations, whereas sites located proximal to the sea with high runoff and high altitude have lower alkalinity concentrations. The three variables selected by the stepwise method provide a strong statistical (R^2 of 0.673) and process explanation. As before, due to orographic uplift most rainfall (and thus most runoff) occurs at high altitude sites within close proximity to the sea. These sites possess the lowest stream water alkalinity. The high amount of runoff (and rainfall) suggests that S&N deposition is likely to be high in these catchments and short residence times, brought about by thin soils, and low weathering rates, due to the resistant bedrock, are likely to prevail.

Summary

The results from the four regression models (Table 5.6) have given us some insight into the controlling factors of streamwater alkalinity and these are summarised here.

Table 5.6 – Stepwise regression analyses for flow-weighted alkalinity for the full and reduced models.

Model analysed	Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Full model	Intercept	233.30	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-56.00	0.002		39.77
	Distance to Sea (km)	3.03	< 0.001	**68.95**	21.76
	Maximum Altitude (m)	-0.09	0.033		4.06
	THP (% of catchment)	-1.12	0.047		3.36
Geology only	Intercept	98.26	-	**9.29**	-
	SIL (% of catchment)	0.67	0.044		9.29
Geology & Deposition	Intercept	338.80	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-88.00	< 0.001	**46.89**	39.77
	SKS (% of catchment)	-0.73	0.024		7.12
Geology & simple site attributes	Intercept	166.18	-		-
	Distance to Sea (km)	3.38	< 0.001	**67.27**	36.67
	Annual Runoff (m^{-3} yr^{-1})	-0.05	0.003		26.22
	Maximum Altitude (m)	-0.09	0.026		4.38

The low alkalinity streams tend to be high altitude, maritime sites that receive high amounts of rainfall and S&N deposition. In addition, they have leached, thin soils and resistant underlying bedrock. The input of acids into the system along with the low base cation resupply from the soils and bedrock are the primary reasons for these sites possessing low streamwater alkalinity. In contrast, the high alkalinity streams tend to receive low rainfall and S&N deposition and be located large distances from the sea at low altitudes. The primary reason for these sites possessing high streamwater alkalinity is that the base cation resupply is probably high (from the underlying base-rich bedrock and thick soils) and can buffer any input of acids from the atmosphere.

A relatively high R^2 value for alkalinity (0.656) was provided by the first three independent variables selected by the stepwise method when the full model was used. The strength of this statistical association suggests that these simple catchment characteristics may be able to predict streamwater alkalinity over a broad chemical gradient. This is discussed in the following section (Section 5.2.2c), where several simple water quality models are created for predicting alkalinity concentrations within the Lake District data.

c. Usefulness of catchment variables for predicting streamwater alkalinity

This section explores the possibility of creating a simple predictive water quality model for alkalinity using the full model of catchment variables. This process involved the development of regression models based on a subset of the data to predict alkalinity concentrations in the remaining subset. The purpose of this exercise was to ascertain whether: (a) there is any bias in the subsets of data; (b) the variables selected during the previous section's regression models are selected again (i.e. are our insights into the important governing processes correct); and (c) the empirical model can successfully predict alkalinity with known confidence intervals.

The regression models were tested for their predictive capability and possible bias by splitting the data in half using a random number generator. In addition, two-thirds (i.e. n = 33) of the data were randomly selected with a random number generator. Stepwise regression models were developed using the first randomly selected subset of streams (Table 5.7). The explanations (i.e. R^2 values) offered by the regression models were then compared to the previous model to assess whether any bias transpires in the two subsets of data.

Table 5.7 – Predicting alkalinity concentrations using the full stepwise regression models.

Attempt No.	Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
First attempt (50:50 split)	Intercept	96.33	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-24.93	0.022		42.40
	Distance to Sea (km)	4.61	< 0.001	**73.08**	23.79
	Maximum Altitude (m)	-0.11	0.046		6.79
Second attempt (50:50 split)	Intercept	194.56	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-32.10	0.013	**79.10**	46.85
	Distance to Sea (km)	3.97	< 0.001		23.39
	Maximum Altitude (m)	-0.16	0.013		8.86
Third attempt (66:33 split)	Intercept	234.31	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-78.97	< 0.001	**64.22**	46.38
	Distance to Sea (km)	2.68	0.001		18.84

First data split

Using half the data, the stepwise regression method selected S&N deposition, distance to sea and maximum altitude as independent variables and accounts for approximately 73% of the variation in the alkalinity concentrations (Table 5.7). The regression model has selected the same variables with similar coefficient direction as the full model (Section 5.2.2b). This suggests that our insights into the important governing processes are correct and that we should be able differentiate between low and high alkalinity sites on the basis of their catchment characteristics.

Second data split

Using half the data generated from another random series, the stepwise regression method selected S&N deposition, distance to sea and maximum altitude as independent variables and accounts for approximately 79% of the variation in the alkalinity concentrations (Table 5.7). This suggests that this subset of data has by chance excluded sites that deviate more from the empirical relationships determined in the full model (with R^2 of 0.69). That is, the random method selected catchments that were disproportionately similar.

Again, the regression model has selected the same variables with similar coefficient direction as the full model (Section 5.2.2b), suggesting that we should be able differentiate between low and high alkalinity sites on the basis of their catchment characteristics.

Third data split

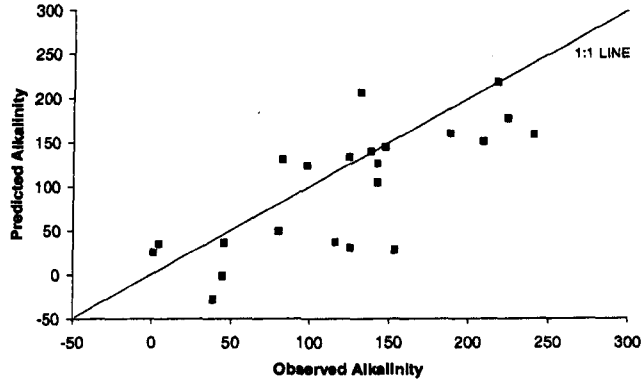
Using two-thirds of the data generated from another random series, the stepwise regression method selected S&N deposition and distance to sea as independent variables and accounts for approximately 64% of the variation in the alkalinity concentrations (Table 5.7). Compared with the full model (Section 5.2.2b), the regression model has selected two of the same variables with similar coefficient direction. However, the new model has discarded maximum altitude, which was the least highly correlated variable in the full model. This suggests that maximum altitude may not be as important for predicting streamwater alkalinity concentrations, but we should still be able to differentiate between low and high alkalinity sites on the basis of their distance from the sea and S&N deposition.

The fact that the same variables were selected as previously, accompanied by the strength of the statistical association, suggests that these models are relatively robust and that the variables chosen – S&N deposition, distance to sea and maximum altitude – are good candidates for predicting alkalinity at new sites. These prediction 'attempts' are discussed in the following section.

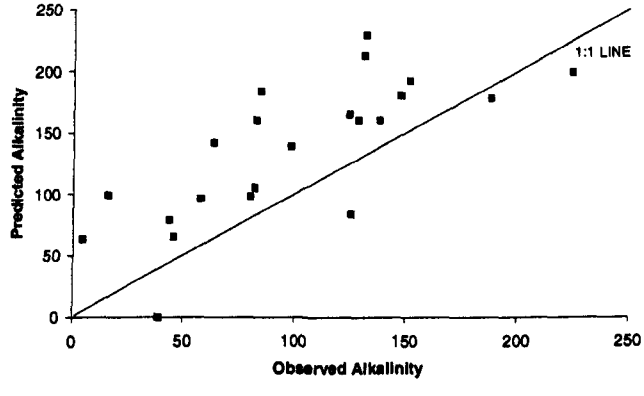
Do the empirical models successfully predict alkalinity within large confidence limits?

The split data regression models from Table 5.7 were used to predict the alkalinity concentrations of the remaining randomly selected streams (Figure 5.1).

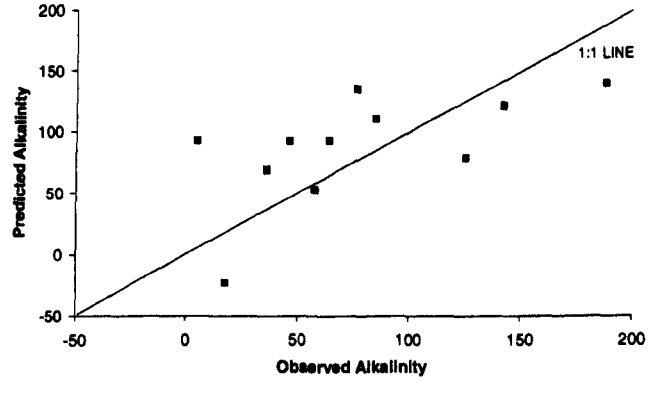
Figure 5.1 – Predicting alkalinity concentrations using the models developed in Table 5.7.
(a) 1st attempt – using model developed on 22 sites to predict the concentrations in remaining 22 sites
(b) 2nd attempt – using model developed on 22 sites to predict the concentrations in remaining 22 sites
(c) 3rd attempt – using model developed on 33 sites to predict the concentrations of remaining 11 sites



(a)



(b)



(c)

The first data split used S&N deposition, distance to sea and maximum altitude to predict alkalinity concentrations and results in a reasonably close agreement between predicted and observed values as most of the predicted values are within 50 μeq l^{-1} of the 1:1 line (Figure 5.1a). To test the statistical strength of the three-variable model's predictive capabilities, the relationship between the predicted and observed values was determined using simple bivariate regression. The model resulted in a R^2 value of 0.559 (56%), which, considering the complexity of the processes involved in streamwater chemistry, is a fairly good approximation of the alkalinity in Lake District streams.

The second data split also used S&N deposition, distance to sea and maximum altitude to predict alkalinity concentrations and resulted in a reasonably close agreement between predicted and observed values (Figure 5.1b). The model (R^2 value of 0.552) produces a fairly good approximation of the alkalinity in Lake District streams, as most of the predicted values are within 50 μeq l^{-1} of the 1:1 line. However, the majority of the predictions are high and it is possible (using Figure 5.1b and Table 5.7) to suggest that the second data split contained disproportionately similar catchments (i.e. the split wasn't even among all the groups). Therefore, the remaining sites almost all show lower alkalinity than the predicted value. This may be important later on in the thesis, as the same problems may arise when the model is extrapolated to sites that have somewhat different composition than the model sites.

The third data split (66:33) used S&N deposition and distance to sea to predict alkalinity concentrations and resulted in a greater degree of scatter between the predicted and observed values, although most of the predicted values were still within 50 μeq l^{-1} of the 1:1 line (Figure 5.1c). The model produced a R^2 value of 0.363 (36%) probably due to there being too few streams left for predictive purposes.

Summary

Although many complex processes control streamwater chemistry, the empirical models created in this section provide an approximation of alkalinity to ± 50 μeq l^{-1} using only three simple catchment characteristics. Therefore, it should be possible to use the model to predict alkalinity concentrations in Lake District streams within about 50 μeq l^{-1} using these characteristics as long as the streams have relevant catchment parameters within the range of the initial model. In addition, the statistical relationship between S&N deposition and alkalinity may allow predictions of how alkalinity may change with changing S&N deposition in the future (c.f. Section 5.5).

d. Insights into the controlling factors of streamwater calcium, pH and nitrate gained from stepwise multiple regression results

In addition to highlighting the factors controlling alkalinity, I wished to gain some insight into the factors controlling other streamwater determinands. Using the same approach as before (i.e. catchment variables in a stepwise multiple regression), this sub-section attempts to give some insight into the controlling factors of calcium, pH and nitrate in streamwater.

Calcium

Using the full model results in four statistically significant independent variables (annual runoff, distance to sea, UPL and S&N deposition) being selected to account for the highest amount of variation (R^2 of 0.709) in calcium concentrations (Table 5.8). The results of the other models can also be found in Table 5.8. The 'geology only' model (R^2 of 0.229) selects one variable (SIL), the 'geology and deposition' model (R^2 of 0.386) selects two variables (S&N deposition and SIL), and the 'geology and simple site attribute' model (R^2 of 0.679) selects four variables (annual runoff, distance to sea, site altitude and SIL).

Table 5.8 – Stepwise regression analyses for flow-weighted calcium for the full and reduced models.

Model analysed	Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Full model	Intercept	151.69	-		-
	Annual runoff (m^{-3} yr^{-1})	-0.14	0.004		31.91
	Distance to sea (km)	3.61	< 0.001	**70.88**	24.65
	UPL (% of catchment)	-0.89	0.001		10.93
	S&N Deposition (keq ha^{-1} yr^{-1})	101	0.04		3.39
Geology only	Intercept	139.77	-	**22.85**	-
	SIL (% of catchment)	0.98	0.001		22.85
Geology & Deposition	Intercept	289.74	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-56.44	0.002	**38.57**	30.85
	SIL (% of catchment)	0.62	0.029		7.72
Geology & simple site attributes	Intercept	176.45	-		-
	Annual Runoff (m^{-3} yr^{-1})	-0.05	0.001		31.91
	Distance to Sea (km)	3.66	< 0.001	**67.91**	24.65
	Site Altitude (m)	-0.22	0.031		7.98
	SIL (% of catchment)	0.45	0.05		3.37

The full model (Table 5.8) suggests that the most highly correlated variables to flow-weighted calcium are annual runoff, which accounts for approximately 32% of the variation, distance to sea (24% of the additional variation) and UPL (11% of the additional variation). S&N deposition is less highly correlated with the stream's calcium, accounting for approximately 3% of the additional variation when the 3 other variables are in the model. The direction of the coefficients suggests that sites with low runoff, located large distances from the sea and low proportions of 'upland' land cover (i.e. high proportions of forestry and/or agriculture) should have high calcium concentrations. The final variable, S&N deposition, accounts for only 3% of the additional variation in the model and is the only variable that does not afford a ready explanation since it is positively correlated to calcium in the model. When no other variables are considered, calcium is high in sites receiving low S&N deposition (Section 4.3.2b), therefore it is likely to be a statistical artefact.

The 'geology only' model suggests that SIL has the highest correlation with calcium (23% of the variation). The direction of the coefficient suggests that sites underlain by Silurian Slates have relatively high calcium concentrations and other bedrock types have lower concentrations. The geochemical data (Section 4.3.2b) support this idea, as the easily weathered Silurian Slates are likely to have the highest base cation resupply rates.

The 'geology and deposition' model suggests that the most highly correlated variables to streamwater calcium are S&N deposition (31% of the variation) and SIL (8% of the additional variation). The direction of the coefficients infer, as is sensible, sites receiving low S&N deposition and underlain by Silurian Slates have low calcium concentrations.

The 'geology and simple site attribute' model suggests that the most highly correlated variables to calcium concentrations are annual runoff (32% of the variation) and distance to sea (25% of the additional variation). Site altitude and SIL are less highly correlated with the stream's calcium concentrations, accounting for 8% and 3% of the additional variation respectively. Using the direction of the coefficients to infer the difference between low and high calcium sites results in a fairly sensible pattern. They suggest that low runoff sites, located relatively far from the sea and/or at low altitudes, underlain by Silurian Slates should have high calcium concentrations. The four variables selected by the stepwise method have provided a strong statistical (R^2 of 0.679) explanation, which may be sensibly linked to processes.

High calcium streams tend to be low altitude, inland sites that receive low amounts

of rainfall and S&N deposition. In addition, they probably have thick soils and easy weathered underlying bedrock. The low input of acids into the system along with the high base cation resupply from the soils and bedrock are the primary reasons for these sites possessing high calcium concentrations. In contrast, the low calcium streams tend to receive high rainfall and S&N deposition and be located close to the sea at high altitudes. The primary reason for these sites possessing low calcium concentrations is that the base cation resupply is frequently low (due resistant bedrock and thin, leached soils) and cannot buffer the high input of acids from the atmosphere.

pH

Using the full model results in three statistically significant independent variables (S&N deposition, SKS and distance to sea) being selected to account for the highest amount of variation (R^2 of 0.613) in pH (Table 5.9). The results of the other models can also be found in Table 5.9. The 'geology only' model (R^2 of 0.176) selects one variable (SKS), the 'geology and deposition' model (R^2 of 0.546) selects two variables (S&N deposition and SKS), and the 'geology and simple site attribute' model (R^2 of 0.614) selects three variables (annual runoff, SKS and distance to sea).

Table 5.9 – Stepwise regression analyses for flow-weighted pH for the full and reduced models.

Model analysed	Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Full model	Intercept	7.48	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-0.39	< 0.001		36.55
	SKS (% of catchment)	-0.006	< 0.001	**61.31**	18.01
	Distance to Sea (km)	0.009	0.012		6.75
Geology only	Intercept	6.73	-	**17.62**	-
	SKS (% of catchment)	-0.006	0.005		17.62
Geology & Deposition	Intercept	7.86	-		-
	S&N Deposition (keq ha^{-1} yr^{-1})	-0.44	< 0.001	**54.56**	36.55
	SKS (% of catchment)	-0.006	< 0.001		18.01
Geology & simple site attributes	Intercept	7.44	-		-
	Annual Runoff (m^{-3} yr^{-1})	-0.0004	< 0.001	**61.40**	32.87
	SKS (% of catchment)	-0.006	< 0.001		19.95
	Distance to Sea (km)	0.01	0.005		8.58

The full model (Table 5.9) suggests that the most highly correlated variables with pH are S&N deposition (36% of the variation) and SKS (18% of the additional variation). Distance to sea is less highly correlated with the stream's pH, accounting for approximately 7% of the additional variation when the other two variables are in the model. The direction of the coefficients suggests that sites that are underlain by Skiddaw Slates with high S&N deposition and/or close to the sea should possess a low pH. The geochemical data (Section 4.3.2b) and our knowledge support this idea, as the base-poor Skiddaw Slates usually are associated with low pH streams and the pH of streams is often lower in maritime and/or high altitude areas.

The 'geology only' model suggests that SKS has the highest correlation with streamwater calcium concentrations (18% of the variation). The direction of the coefficient suggests that streams draining sites underlain by Skiddaw Slates have low pH values. The geochemical data (Section 4.3.2b) and our knowledge support this idea, as the Skiddaw Slates weather poorly and provide low base cation resupply rates.

The 'geology and deposition' model suggests that the most highly correlated variables to streamwater pH are S&N deposition (31% of the variation) and SKS (18% of the additional variation). The direction of the coefficients infer that sites receiving high S&N deposition and underlain by Skiddaw Slates have relatively low pH values.

The 'geology and simple site attribute' model suggests that the most highly correlated variables to pH are annual runoff (33% of the variation) and SKS (20% of the additional variation). Distance to the sea is less highly correlated with the stream's pH, accounting for 9% of the additional variation when the other two factors are considered in the model. Using the direction of the coefficients to infer the difference between low and high pH sites results in a logical pattern. They suggest that high runoff sites underlain by Skiddaw Slates located close to the sea should have low pH values. Therefore, the three variables selected by the stepwise method have provided a reasonable process explanation, as well as a strong statistical (R^2 of 0.614) explanation.

Low pH streams tend to be underlain by Skiddaw Slates. They also tend to be close to the sea and receive high S&N deposition because of their high altitude. The base cation resupply is probably low (due resistant bedrock and thin, leached soils) and cannot buffer the high input of acids from the atmosphere. This is the primary reason for the low pH of these sites. In contrast, high pH streams tend to be large distances from the sea and receive low loads of S&N deposition. They also possess thicker soils and easy weathered bedrock (high base cation resupply) which more easily buffers the low input of acids into the system.

Nitrate

The multiple regression models for nitrate use the flow-weighted data from all the sites (N = 55) as agriculture is an important control of nitrate concentrations in the streams (Section 4.3). Using the full model results in two statistically significant independent variables (AGR and THP) being selected to account for the highest amount of variation (R^2 of 0.451) in nitrate concentration (Table 5.10). The results of the other models can also be found in Table 5.10. The 'geology only', the 'geology and deposition' and the 'geology and simple site attribute' models (R^2 of 0.236) all select the same variable (SIL).

Table 5.10 – Stepwise regression analyses for flow-weighted nitrate for the full and reduced models (including agriculture sites – N=55).

Model analysed	Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Full model	Intercept	0.95	-		-
	AGR (% of catchment)	0.47	0.006	**45.11**	39.89
	THP (% of catchment)	0.59	0.031		5.22
Geology only	Intercept	8.41	-	**23.6**	-
	SIL (% of catchment)	0.40	< 0.001		23.6
Geology & Deposition	Intercept	8.41	-	**23.6**	-
	SIL (% of catchment)	0.40	< 0.001		23.6
Geology & site attributes	Intercept	8.41	-	**23.6**	-
	SIL (% of catchment)	0.40	< 0.001		23.6

The full model (Table 5.10) suggests that the most highly correlated variable is AGR (40% of the variation). THP is less highly correlated with the stream's nitrate concentrations, accounting for approximately 5% of the additional variation. The direction of the coefficients suggests that sites dominated by agriculture and underlain by THP soil (positive coefficients) should possess high nitrate concentrations. From our knowledge of the sites we know that streams with high nitrate concentrations are usually dominated by agriculture and/or underlain by THP soils. However, the geochemical data (Section 4.3.2b) tends to support the idea that agriculture rather than soil type exerts the main influence on the streams nitrate concentrations.

The 'geology only', 'geology and deposition' and the 'geology and simple site attribute' models suggest that SIL has the highest correlations with nitrate concentrations (24% of the variation). The direction of the coefficient suggests that sites underlain by

Silurian Slates have high nitrate concentrations. There is no obvious explanation why a difference in bedrock should result in different nitrate concentrations. However, since all of the agriculture occurs on Silurian Slate bedrock, it is likely that agriculture rather than bedrock is the main control of stream nitrate. In Chapter 4, the Silurian Slate group was split into 'with agriculture' and 'non-agriculture' sites because the geochemical data suggested agriculture was overriding all the other processes controlling water chemistry (Section 4.3.2b).

High nitrate streams tend to be underlain by Silurian Slates and/or THP soils with dominant agricultural land use. The relationship between Silurian Slates and elevated nitrate concentrations is likely spurious as all the catchments are agriculture-dominated. Therefore, the high nitrate concentrations are probably a product of the agricultural land use and the soil rather than bedrock type.

Summary

The results from the regression models have given us some insight into the factors controlling streamwater calcium, pH and nitrate. For example, high calcium and pH streams tend to be low altitude, inland sites that receive low amounts of rainfall and S&N deposition and possess thick soils and easy weathered underlying bedrock. The primary reason for these sites possessing high calcium and pH concentrations is likely to be the high base cation resupply from the soils and bedrock, along with the low input of acids into the system. Low calcium and pH streams, in contrast, have a low base cation resupply (due resistant bedrock and thin, leached soils) which is unable to buffer the high input of acids from the atmosphere. In contrast, high nitrate streams tend to be the product of the agricultural land use.

5.2.3. Relationships between water chemistry and catchment characteristics using principal component modelling

The conceptual basis behind principal component analysis (PCA), an unconstrained ordination technique, is fully described in Section 2.5.1b, where it is shown that PCA evaluates the correlation structure between variables. PCA is often used as a data reduction technique, as it can reduce the number of variables entered into the model by identifying groups of variables that behave in a similar fashion.

The PCA results are interpreted by looking at i) the proportion of the variance

associated with each principal component and ii) the correlation of the variables (loading) with each PCA axis. However, it is often easier to interpret the results by plotting the loadings of the PCA axes on a correlation biplot. The vectors on the correlation biplot point in the direction of maximum variation and their length is proportional to the variation. Bearing this in mind, arrowheads furthest from the origin are the most important indicators of site variation, whilst those nearest the origin are of less importance. Vectors which display acute angles are positively correlated and those with obtuse angles have negative correlations (TerBraak, 1983). Inferences are attempted as to what each PCA axis may represent in terms of catchment processes or stream character, but it should be noted that like multiple regression, PCA cannot establish cause and effect.

a. Water chemistry PCA

PCA was undertaken on the water chemistry variables using flow-weighted data from 44 non-agricultural sites. The PCA results for the water chemistry variables are presented in Table 5.11.

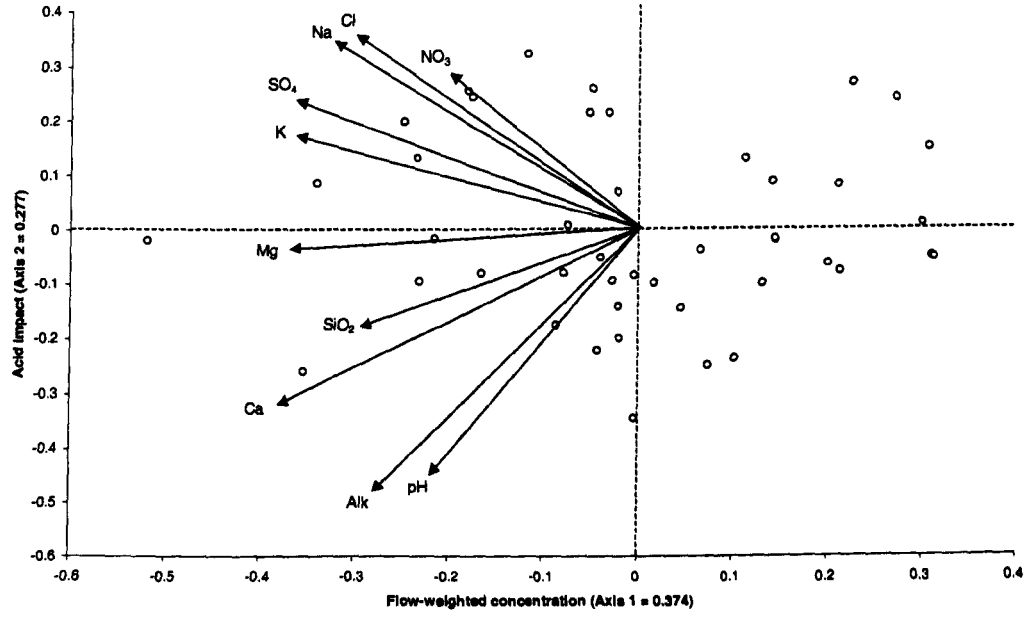
Table 5.11 – Results of PCA on 10 flow-weighted water chemistry variables
(excluding agricultural sites – N=44)

	PCA Axes			
	1	2	3	4
Eigenvalue	3.7423	2.7723	1.0416	0.7336
Proportion	0.374	0.277	0.104	0.073
Cumulative % variance	0.374	0.651	0.756	0.829
Variable loadings (correlations)				
pH	-0.221	-0.456	-0.153	0.208
Sodium	-0.324	0.345	0.275	0.011
Magnesium	-0.371	-0.035	0.605	0.101
Calcium	-0.382	-0.323	-0.211	0.283
Potassium	-0.366	0.172	0.256	-0.142
Chloride	-0.300	0.355	-0.192	-0.059
Nitrate	-0.204	0.289	-0.570	-0.068
Sulphate	-0.363	0.240	-0.220	0.378
Alkalinity	-0.276	-0.484	-0.016	-0.005
Silica	-0.297	-0.189	-0.116	-0.834

Approximately 37% of the variance associated with the water chemistry concentrations can be explained by the first PCA axis. The second axis is responsible for an

additional 28% of the variation, and axes 3 and 4 explain an additional 10% and 7% respectively. The first four axes explain 83% of the total variation in the chemical data, of which the first two axes explain 65%. The correlations in the first axis most likely represent the variation in the water chemistry and are relatively unimportant to our interpretation. Axis 2 shows the highest positive correlations with chloride (0.355), sodium (0.345) and nitrate (0.289) and the highest negative correlations with alkalinity (-0.484), pH (-0.456) and calcium (-0.323). Axis 3 shows the highest positive correlations with magnesium (0.605) and the highest negative correlations with nitrate (-0.570). Axis 4 shows the highest positive correlations with sulphate (0.378) and the highest negative correlations with silica (-0.834). The interpretation of these patterns becomes easier when they are presented on a correlation biplot. The ordination loadings of the first two PCA axes are plotted in Figure 5.2 to illustrate the patterns quantified in Table 5.11.

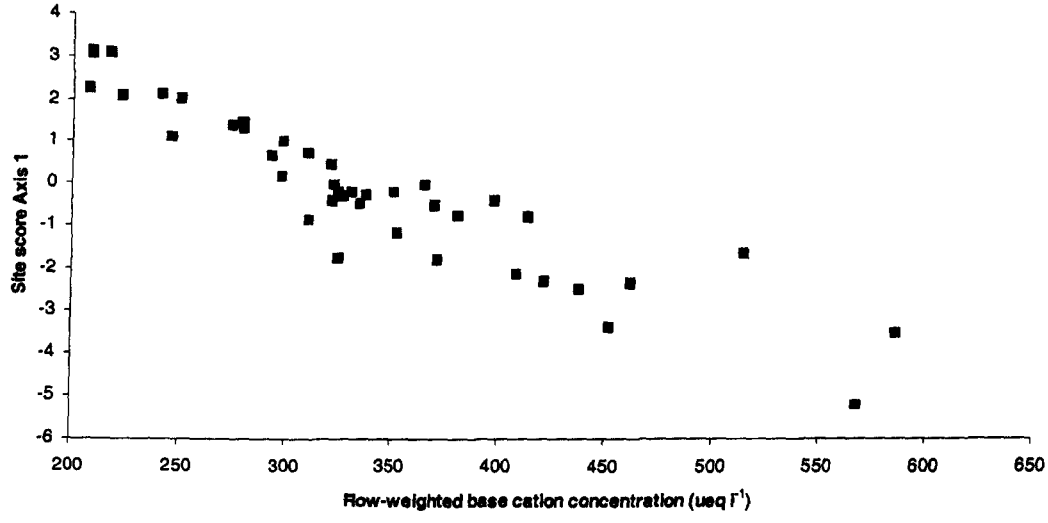
Figure 5.2 - Correlation biplot of 10 flow-weighted water chemistry variables
(excluding agricultural sites – N=44)



The chemical data plot in the same direction and display a similar magnitude with the first axis. This axis possibly represents the water chemistry concentrations of the study streams. Therefore, the sites with the highest positive scores on axis 1 are characterised by lowest concentrations whereas the negative scores have higher concentrations. Therefore, the concentration decreases from left to right across the plot. This is further illustrated by

plotting flow-weighted base cations against the site scores from PCA axis 1 (Figure 5.3).

Figure 5.3 - Scatterplot of flow-weighted alkalinity against the site scores of PCA axis 1



Along the second axis, alkalinity, pH, calcium, magnesium and silica display negative values (PCA axis 2 loading of -0.035 to -0.484) and sodium, chloride, nitrate, sulphate and potassium have positive values (PCA axis 2 loading of 0.172 to 0.355). The high negative correlations for pH, silica and alkalinity, in conjunction with the high positive correlations for chloride, sodium and nitrate suggest that this axis possibly represents the impact of acid deposition. For example, the well-buffered sites will have high pH, alkalinity and silica and low acid anions and sea-salt influence, whereas sensitive sites will have high acid anions and sea-salt and low pH, alkalinity and silica.

Summary

Some water chemistry variables 'emerge together' in the PCA models. For example, the 'positive' variables (chloride, sodium, sulphate and nitrate) and 'negative' variables (pH, silica, calcium and alkalinity) on PCA axis 2 might be associated with the sites sensitive to acidification.

b. Catchment characteristics PCA

The PCA results for 18 catchment characteristic variables (i.e. geology, soil and land use categories, S&N deposition, annual rainfall and runoff, site and maximum altitude and distance from the sea) are presented in Table 5.12.

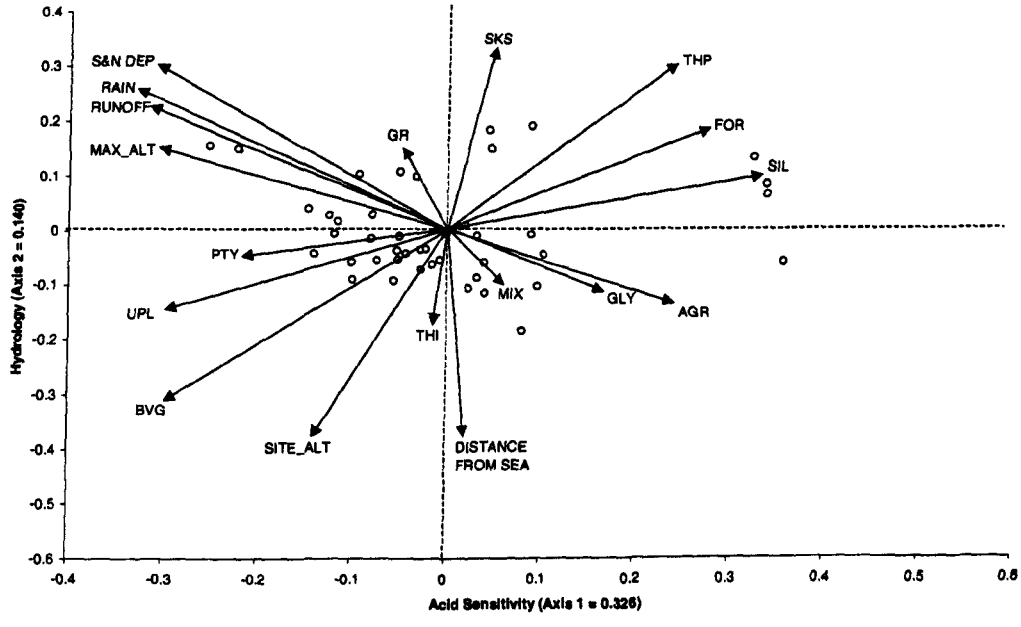
Table 5.12 – Results of PCA on 18 catchment characteristic variables
(excluding agricultural sites – N=44)

	PCA Axes			
	1	2	3	4
Eigenvalue	5.8593	2.5119	2.3744	1.8656
Proportion	0.326	0.140	0.132	0.104
Cumulative % variance	0.326	0.465	0.597	0.701
Variable loadings (correlations)				
BVG	-0.298	-0.316	-0.142	-0.240
SKS	0.051	0.339	0.403	0.204
SIL	0.336	0.101	-0.173	0.110
MIX	0.059	-0.100	0.119	0.422
GR	-0.049	0.163	-0.016	-0.264
UPL	-0.306	-0.147	0.356	-0.001
FOR	0.278	0.183	-0.372	0.039
AGR	0.240	-0.138	-0.029	-0.186
THP	0.243	0.297	0.388	0.120
THI	-0.018	-0.184	0.217	-0.475
GLY	0.169	-0.115	0.200	-0.262
PTY	-0.219	-0.047	-0.446	0.277
S&N Deposition	-0.316	0.309	-0.063	-0.040
Annual Rainfall	-0.331	0.260	-0.075	0.014
Annual Runoff	-0.320	0.234	-0.029	-0.031
Site altitude	-0.143	-0.374	0.111	0.384
Maximum altitude	-0.304	0.155	0.182	0.079
Distance to sea	0.021	-0.382	0.121	0.253

Approximately 33% of the variance associated with the 18 independent variables from the full dataset can be explained by the first PCA axis. The second axis is responsible for an additional 14% of the variation, and axes 3 and 4 explain an additional 13% and 10% respectively. The first four axes explain 70% of the total variation in the chemical data, of which the first two axes explain 47%. Axis 1 shows the highest positive correlations with SIL (0.336), FOR (0.278), THP (0.243) and AGR (0.240) and the highest negative correlations with annual rainfall (-0.331), annual runoff (-0.320), S&N deposition (-0.316), UPL (-0.306), maximum altitude (-0.304) and BVG (-0.298). Axis 2 shows the highest positive correlations with SKS (0.339), S&N deposition (0.309) and THP (0.297) and the highest negative correlations with distance from the sea (-0.382), Site altitude (-0.374) and

BVG (-0.316). Axis 3 shows the highest positive correlations with SKS (0.403), THP (0.388) and UPL (0.356) and the highest negative correlations with PTY (-0.446) and FOR (-0.372). Axis 4 shows the highest positive correlations with MIX (0.422) and Site altitude (0.384) and the highest negative correlation with THI (-0.475). The ordination loadings for the first two PCA axes are plotted in Figure 5.4 to illustrate the patterns quantified in Table 5.12.

Figure 5.4 - Correlation biplot of 18 catchment characteristic variables (excluding agricultural sites – N=44)



The vectors for Silurian Slate bedrock, thick, permeable soil, forested and agricultural land use exhibit a similar magnitude in a positive direction on axis 1 (PCA axis 1 loading of 0.240 to 0.336). On the negative side of axis 1, the vectors for S&N deposition, annual rainfall, annual runoff, maximum altitude, upland land use and Borrowdale Volcanic bedrock exhibit a similar magnitude (PCA axis 1 loading of -0.298 to -0.331). The high positive correlations for SIL, THP, AGR and FOR, in conjunction with the high negative correlations for S&N deposition, annual rainfall and runoff, maximum altitude, UPL and BVG might suggest that this axis represents an index of acid sensitivity. Given the way that certain variables group together, along with the high correlations, it may be possible to characterise sites along the sensitivity gradient. For example, the highest positive scores on

axis 1 might represent lowland catchments underlain by Silurian Slates with thick soils, dominant agriculture and forestry that have low runoff and receives low rainfall and S&N deposition. Sites showing negative scores are high altitude catchments underlain by Borrowdale Volcanics and peaty soil, with dominant upland vegetation which receive elevated rainfall and S&N deposition. Therefore, a gradient showing the sensitivity to acidification might go from left (highly sensitive) to right (less sensitive) on the plot.

Along the second axis, BVG, MIX, AGR, THI, GLY, PTY, Site altitude and distance from the sea display negative values (-0.047 to -0.382) and SIL, SKS, GR, FOR, THP, S&N deposition, annual rainfall, annual runoff and maximum altitude have positive values (0.101 to 0.339). The high negative correlations for distance from the sea, site altitude and BVG, in conjunction with the high positive correlations for SKS, S&N deposition and THP might suggest that this axis possibly represents the hydrological character of the streams rather than a chemical process.

Summary

Some independent variables 'emerge together' in the PCA models. For example, four variables (Silurian Slates, forestry, agriculture and thick soil) are usually associated with sites that are less sensitive to acidification (i.e. high alkalinity sites). Six variables (Borrowdale Volcanics, upland vegetation, maximum altitude, high S&N deposition and high annual runoff and rainfall) are associated with sites highly sensitive to acidification (i.e. low alkalinity sites).

One possibility for the predictive model is that the scores from a single principal component (in this case PCA axis 1) could be entered into a regression model. This might provide a potentially useful way of integrating interrelated catchment parameters with streamwater chemistry. However, ten variables is still too many variables for using in a predictive model. Therefore, in the next section (Section 5.2.3c), four independent variables with the largest coefficients were entered into a regression model for predictive purposes.

c. Usefulness of PCA scores for predicting streamwater alkalinity

According to Table 5.12, the four independent variables with the largest coefficients are Silurian Slates, S&N deposition, annual rainfall and annual runoff. PCA was undertaken on these four independent variables and the results are presented in Table 5.13.

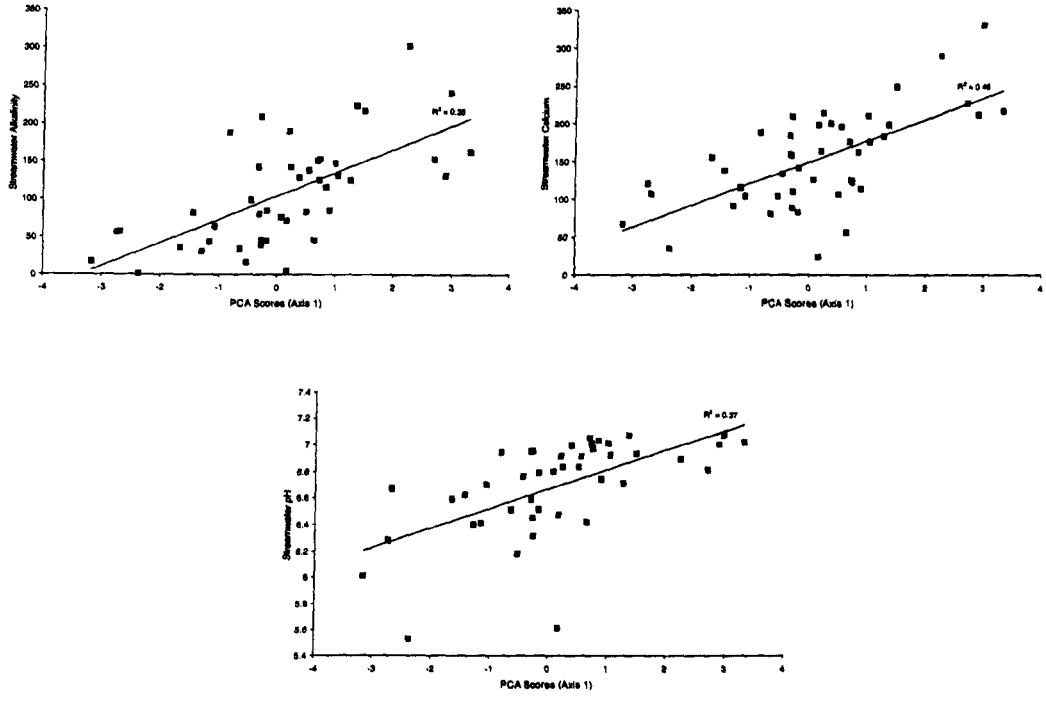
Table 5.13 - Results of PCA on the 4 'most important' independent variables identified from Table 5.12

	PCA Axes			
	1	2	3	4
Eigenvalue	3.1636	0.7565	0.0610	0.0189
Proportion	0.791	0.189	0.015	0.005
Cumulative % variance	0.791	0.980	0.995	1.000
Variable loadings (correlations)				
SIL	0.319	-0.947	0.028	0.028
S&N Deposition	-0.549	-0.212	-0.106	-0.802
Annual Rainfall	-0.546	-0.188	-0.639	0.508
Annual Runoff	-0.547	-0.152	0.761	0.314

Approximately 79% of the variance associated with the four independent variables can be explained by the first PCA axis. The second axis is responsible for an additional 19% of the variation, and axes 3 and 4 explain an additional 1.5% and 0.5% respectively. The first two axes explain 98% of the total variation in the chemical data. Axis 1 shows similar magnitude negative correlations with three of the variables, S&N deposition (-0.549), annual rainfall (-0.546) and annual runoff (-0.547), and exhibits a positive correlation with SIL (0.319).

Although PCA scores take no account of the various processes and interactions within the catchment, they may still provide an adequate method of predicting water chemistry. In Section 5.2.3b, it was suggested that the scores from a single principal component (i.e. PCA axis 1) could be entered into a simple bivariate regression in place of the four independent variables. This hypothesis was tested and the relationships between the streamwater concentrations of the alkalinity, calcium and pH and the PCA scores can be found in Figure 5.5.

Figure 5.5 - Using the PCA site scores from axis 1 (Table 5.13) to predict the concentrations of alkalinity, calcium and pH



The predictions produced using the 'PCA scores' model seem to be comparable with the stepwise regression models as the relationship with alkalinity (R^2 of 35%) is fairly similar to the 'split data' models for alkalinity (R^2 of 36-56%). There is also a significant relationship between calcium (R^2 of 48%) and pH (R^2 of 37%) and the PCA scores. Therefore, this method provides a potentially useful way of integrating several intercorrelated catchment parameters with streamwater chemistry.

Summary

PCA predictions were comparable to the multiple regression predictions. However, they fall at the low end of the relative R^2 range. The models could still be used to predict streamwater concentrations of alkalinity, calcium and pH. However, the alkalinity is within ± 100 $\mu eq\ l^{-1}$ compared to ± 50 $\mu eq\ l^{-1}$ when the multiple regression models were used. Therefore, probably the best way to use these models is as a data reduction technique, as it can reduce the number of variables entered into the model by identifying groups of variables that behave in a similar fashion. A useful way of using PCA would be to confirm whether our inferences about each axis (and the process it represents) are correct.

d. Summary

Empirical models are based upon statistical analysis and take no account of the various processes and interactions within a catchment that govern streamwater chemistry. However despite the complexity of stream processes / interactions and the low data requirements, alkalinity concentrations of Lake District streams have been predicted within about 50 $\mu eq\ l^{-1}$ using the simple models presented in this section. Therefore, it is important not to underestimate the worth of these results, which have provided an adequate approximation of alkalinity using only three or four simple catchment characteristics.

The next section (Section 5.3) uses process-based modelling to calculate the weathering rates and soil base saturation of the study catchments. This data, along with the weathering patterns derived from critical element ratios (Section 3.5.3), will subsequently be used in a new model that might provide a stronger predictive relationship (Section 5.4).

5.3. Process-based modelling

Process-based models are usually complex and data intensive compared to empirical models. A variety of process-based models have been developed and applied in investigations of surface water quality, some of which were discussed in Section 1.3.3. Dynamic models usually include a substantial empirical element, which simulate theoretical chemical equations (e.g. Gaines-Thomas expression for cation exchange).

In this section, the purposes/uses and advantages/disadvantages of process-based models are briefly discussed to give a background to the modelling undertaken during the study (Section 5.3.1). MAGIC (a process-based model) was applied to the Lake District data (a full description of the model's principles, structure and assumptions can be found in Section 2.5.2) and was undertaken with two objectives:

i. To acquire information about catchment weathering rates using the dynamic element of the process-based model. This information will be compared with weathering proxies based on geology (Section 3.5.3) and should allow us to extrapolate water chemistry into the future and may provide a new way to regionalise water quality prediction.
ii. To estimate background soil base saturation levels to assess the amount of degradation caused by acid deposition.

5.3.1. Purpose/uses and advantages/disadvantages of process-based models

Knowledge and understanding of soil processes is required to predict the response of surface water to changing acid deposition (Jenkins *et al.*, 1997). Most dynamic simulation models utilize simplified mathematical representations of fundamental soil chemical processes like cation exchange, the carbonate-bicarbonate system and weathering kinetics. The process-based approach is a powerful tool for "real-time" predictions. It can predict the extent and timing of changes in stream concentrations. However, a major limitation of dynamic models is the requirement for a large amount of information for a successful application. A scarcity of quality input and output data usually inhibits model calibration and verification. This causes problems for model applications outside the area of calibration. Within the acidification field, there are four process-based models that have been widely utilised: (1) The Integrated Lake-Watershed Study (ILWAS) model (Goldstein *et al.*, 1985); (2) Birkenes model (Seip *et al.*, 1986); (3) PROFILE (Sverdrup and Warfvinge, 1988) and/or SAFE (dynamic version of PROFILE) model (Warfvinge and Sverdrup, 1991); and (4) MAGIC model (Cosby *et al.*, 1984). Research using these models is reviewed in Section 1.3.3.

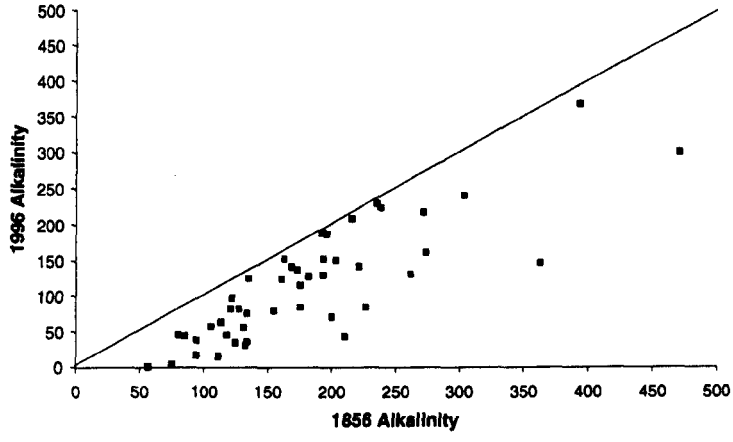
5.3.2. Examination of the soil base saturation and weathering patterns produced for the Lake District streams during the MAGIC calibration

The MAGIC model requires data for surfacewater chemistry, deposition chemistry and volume, soil chemistry and other soil characteristics for calibration and subsequent application. The availability of this data in the UK is subject to licence from the various monitoring organisations. The MAGIC model was only calibrated at forty-four of the survey sites because the sites with dominant agricultural land use were removed. Full details of this calibration and optimisation procedure can be found in Appendix G.

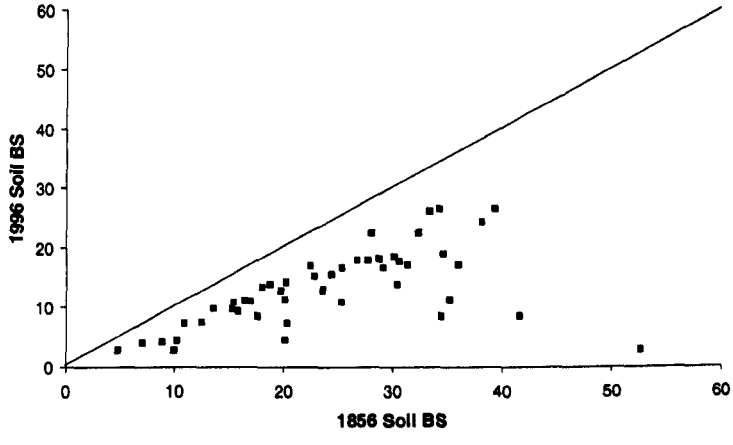
a. Soil base saturation

By comparing the MAGIC simulation of background (i.e. 1856) concentrations of streamwater alkalinity and soil base saturation to present day concentrations, it is possible to assess the level of acidification that has occurred due to an increase in acid deposition and/or land management (Figure 5.6).

Figure 5.6 - Comparison of MAGIC simulated background (1856) and MAGIC simulated present day (1996) chemistry for a) Stream Alkalinity and b) Soil Base saturation. (Units are μeq l^{-1} for alkalinity and % of CEC for base saturation)



a.



b.

The hindcast simulation suggests that alkalinity in the majority of sites has declined dramatically over the last 140 years (Figure 5.6a). The better-buffered sites (> 200 μeq l^{-1} alkalinity) have shown the largest absolute decline, but twelve of the sites have declined to a critical level of sensitivity (< 50 μeq l^{-1} alkalinity) during the last 140 years.

One of the purposes of carrying out the modelling exercise was to assess the decline in soil base saturation due to acid deposition. In general, the sites with the highest observed values of base saturation seem to have lost the most over the 140-year hindcast simulation (Figure 5.15b). However, there are two notable exceptions, Red Dell Beck (Site 7) and Styhead Gill (Site 44). Red Dell Beck's modelled base saturation has declined from 53 % in 1856 simulation to 3 % in 1996, whereas Styhead Gill's modelled base saturation has fallen from 42 % in 1856 to 9 % in 1996. The large decline in modelled base saturation could be

due to acid deposition as these sites receive the highest deposition load (Section 4.2.2). The base cation depletion caused by acid deposition is probably outstripping the base cation resupply from weathering (i.e. progressive acidification). This may have severe ramifications for the stream's ecosystem.

b. Weathering rates

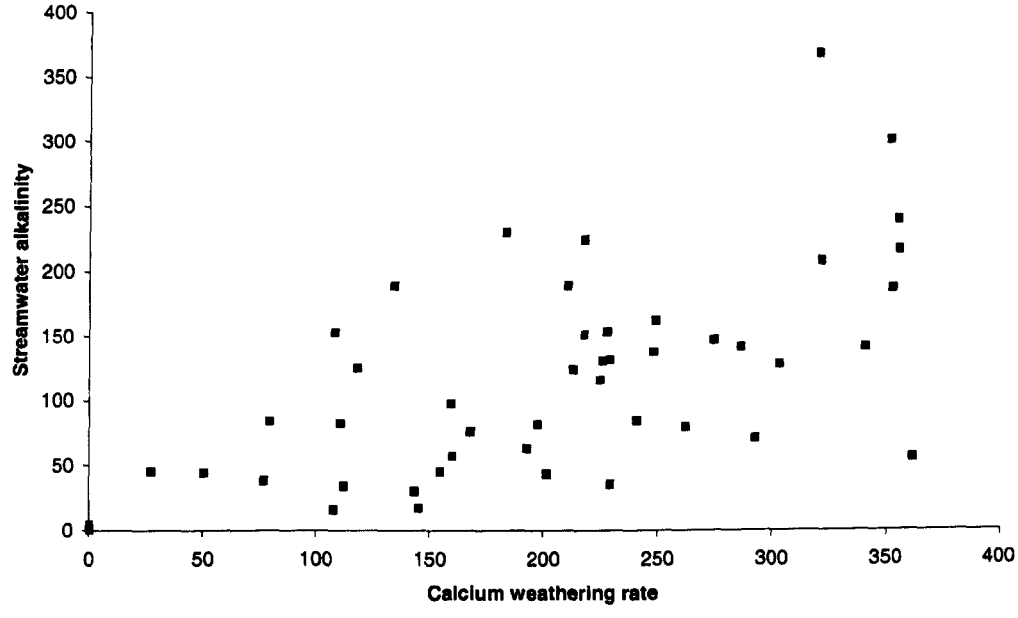
Examining the base cation weathering rates estimated from the optimisation procedure for each catchment (Table 5.14) shows that calcium weathering dominates almost entirely at the expense of the other cations. The dominance of calcium weathering may have implications for streamwater chemistry, primarily as a buffer for acid deposition.

Table 5.14 - Stream alkalinity and MAGIC base cation weathering rates for the 47 optimised sites. (Units are $\mu eq\ l^{-1}$ for alkalinity and $\mu eq\ m^{-2}\ yr^{-1}$ for weathering rates)

Site	Stream Alk	We Ca	We Mg	We Na	We K	Total We
Moasdale Beck	1.1	1	4	69	2	76
Liza Beck	4.28	0	48	35	1	84
Castle How Beck	15.84	108	4	31	0	144
Sour Milk Gill	17.4	145	18	54	0	217
Nether Beck	30.8	143	42	25	1	212
Tarn Beck	34.59	112	47	33	0	192
Whelpside Ghyll	35.98	229	3	36	0	269
Whillan Beck	38.92	77	19	20	1	116
Red Dell Beck	43.46	201	134	70	12	417
Greendale Gill	44.61	50	49	17	0	116
Mill Beck 2	45.36	154	9	0	0	164
Sling Beck	45.72	27	10	28	0	65
Styhead Gill	56.21	362	8	1	3	375
Wyth Burn	57.5	160	0	25	0	185
Launchy Ghyll	63.43	193	0	2	0	194
Coledale Beck	71.11	293	15	0	0	308
Trout Beck	76.04	168	0	29	0	198
Hardknott Gill	79.88	262	0	0	0	262
Glenridding Beck	81.89	197	5	8	0	210
Woundale Beck	82.49	111	5	30	0	145
Stony Beck	84.41	79	15	60	0	155
Rydal Beck	84.6	241	45	1	0	287
Aira Beck	97.88	159	0	6	0	165
Torver Beck	115.84	225	15	7	0	247
Borrow Beck	124.33	213	17	5	1	236
Crosby Gill	125.4	118	12	35	0	165
Shoulthwaite Gill	128.37	303	0	1	0	304
Belle Grange Beck	130.65	226	1	9	0	235
Bannisdale Beck	131.57	229	92	134	1	456
Hagg Gill	137.83	248	3	2	0	253
Stock Ghyll	142.16	341	1	0	0	342
Glencoyne Beck	142.27	286	2	1	0	290
Hall Gill	147.25	275	122	199	0	596
Washfall Beck	151.24	218	23	55	1	296
Holehouse Gill	153.15	108	37	18	0	163
Dale Park Beck	153.3	228	0	5	0	233
River Mint Trib	161.96	249	70	0	3	322
Gatescarth Beck	187.7	353	47	12	0	412
Mosedale Beck	189.32	210	47	0	0	257
Cawdale Beck	189.4	134	27	28	1	190
River Sprint	208.69	321	2	0	1	324
Naddle Beck	217.36	356	27	0	0	383
Fusedale Beck	224.25	218	21	15	0	255
Heltondale Beck	229.91	183	52	36	1	272
Low Cunsey Beck	240.41	355	20	0	0	375
Tailbert Gill	301.8	352	145	104	5	606
Parkhouse Gill	368.45	320	79	54	1	454

Despite the majority of the Lake District stream sites being classified as sensitive to acidification by acid deposition (Section 4.3), the calcium weathering rates seem quite high compared to those found for the two Lake District sites in the Acid Waters Monitoring Network (Jenkins *et al.*, 1997). Table 5.14 does not allow us to examine the relationship between modelled calcium weathering rates and streamwater alkalinity clearly, therefore to aid interpretation the data is presented graphically in Figure 5.7.

Figure 5.7 - Modelled calcium weathering rates compared with streamwater concentrations of alkalinity. (Weathering units are μeq m^{-2} yr^{-1}; streamwater units are μeq l^{-1})



Of the study sites, six sites have stream alkalinities below 100 μeq l^{-1} and calcium weathering rates below 100 μeq m^{-2} yr^{-1} (Sites 1, 26, 29, 33, 34 and 41). Two of these sites, Liza Beck (41) and Moasdale Beck (26), were classified as the most sensitive of the study sites (Section 4.3) and this is reflected by their extremely low modelled calcium weathering rates (< 0.1 and 1 μeq m^{-2} yr^{-1} respectively). In general, an increase in calcium weathering is accompanied by an increase in stream alkalinity. However, the important thing to consider here is not the rate of weathering alone but also the amount of base cation depletion caused by acid deposition. The weathering of rock produces calcium; if the weathering rate is less than the depletion then progressive acidification occurs. Therefore, some of the sites with higher weathering rates receive higher acid deposition loadings, which replaces any cations produced with hydrogen ions and in turn leads to soil acidification. For example, Red Dell

Beck (7) has a relatively high modelled weathering rate for calcium (201 μeq m^{-2} yr^{-1}), a critical alkalinity, and a simulated decline in base saturation from 53% to 3% between 1856 and 1996. The modelled and the chemical data suggest that Red Dell Beck has experienced severe progressive acidification over the past 140 years. The reduction in base status may have implications for the future of the stream's chemistry and associated biota under continued high deposition loadings.

c. Summary

In this study, nine sites (Sites 7, 11, 15, 22, 24, 27, 33, 40 and 55) have experienced a 'modelled' decline in stream alkalinity in excess of 100 μeq l^{-1} between 1856 and 1996. Furthermore, eight sites (Sites 7, 13, 27, 28, 33, 35, 36 and 44) have experienced a 'modelled' base saturation depletion in excess of 15% between 1856 and 1996. There are three sites which experienced both the base saturation and stream alkalinity decline (Sites 7, 27 and 33). The weathering rates at these sites were 417, 144 and 212 μeq m^{-2} yr^{-1} respectively. This indicates, as suggested earlier (Section 5.3.2c), that Red Dell Beck is the most likely site to suffer progressive acidification due to its loss of alkalinity and base status despite a relatively high weathering rate.

The information acquired about the catchment weathering rates is compared with weathering patterns derived from critical element ratios in Section 5.4.1, and an extrapolation of this relationship is used in Section 5.5 to predict future water chemistry.

5.4. Field data and models: An integration of two approaches

To assess whether rock chemistry could be utilised in a new way to predict regional water chemistry I wanted to know if stream chemistry and weathering rates were related in a particular way to the chemistry of the rocks. If they were, then it could be possible to give a rough prediction of the streamwater chemistry using a spot sample of bedrock, thus making the model spatially and temporally applicable.

My hypothesis is that rock weathering patterns derived from critical element ratios (Section 3.5.3) link in a predictable way to streamwater chemistry. The basis for this hypothesis was evidence of strong relationships between the major-ion chemistry and the geological catchment characteristics (Section 4.3), and the ideas of previous studies (For example, Webb, 1984; Lynch and Dise, 1985; Bricker and Rice, 1989) that bedrock and streamwater chemistry are closely inter-related. This hypothesis was tested using a two-

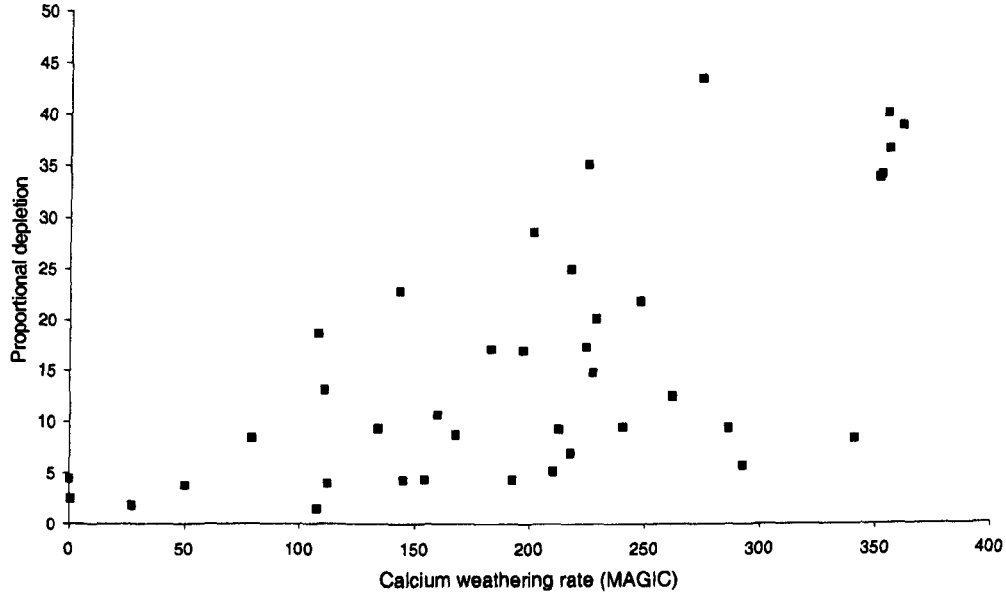
stage approach by attempting to link: (1) the weathering patterns with the optimised weathering rates from MAGIC (Section 5.4.1), and (2) the weathering patterns to surfacewater chemistry (Section 5.4.2).

5.4.1. The links between process-based weathering rates and rock weathering patterns

This phase of the project's modelling aspect attempts to take weathering rates from MAGIC and link them in a predictable way to rock weathering patterns derived using critical element ratios. The rock chemistry work (Section 3.5.3) and the MAGIC weathering rates (Section 5.3.2) are fully described previously in the thesis.

The present study examines a wide range of streams with variable degrees of sensitivity to acidification and a wide range of rock lithologies with variable chemical properties. Calcium dominated almost entirely at the expense of the other cations in the process-based modelling section (Section 5.3.2b – Table 5.14). Therefore, modelled calcium weathering rates of the sites were examined in relation to the weathering patterns produced in Section 3.5.3 to assess whether a relationship exists between lithology and modelled weathering rates (Figure 5.8)

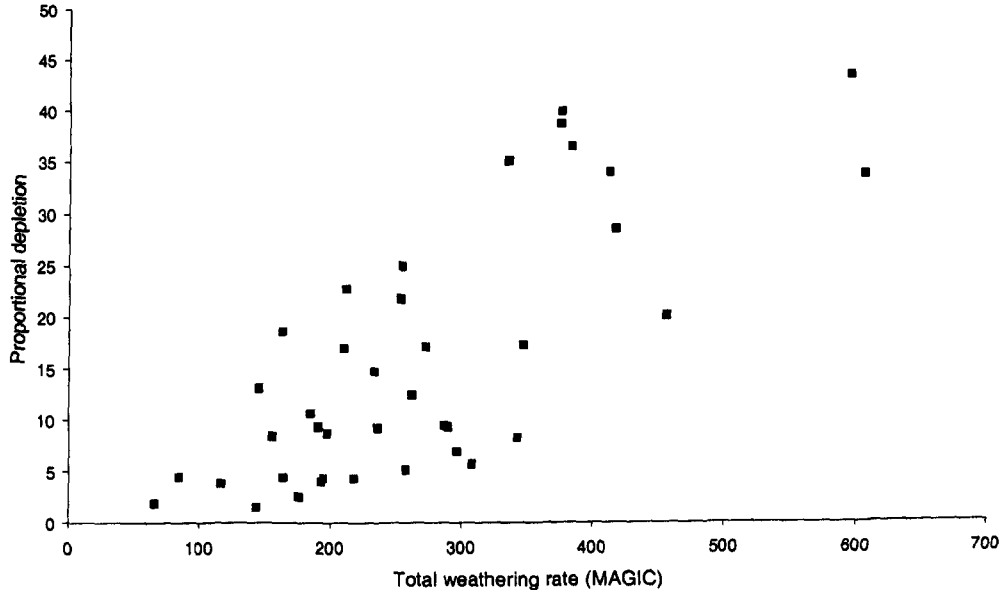
Figure 5.8 - Examining the relationships between modelled calcium weathering rates and weathering patterns derived from critical element ratios.
(Units are μeq m^{-2} yr^{-1} for weathering rates and % depletion of the Sr/Zr ratio between fresh and weathered rock samples for the weathering patterns)



The modelled weathering rates show a positive trend with the weathering patterns derived from critical element ratios (Figures 5.8), which suggests that there is a significant relationship between them. To test the statistical strength of this relationship, the modelled calcium weathering rates and the weathering patterns were entered into a simple bivariate regression, which resulted in a R^2 value of 0.425 (43%). Considering that the strontium loss from rocks is usually a good proxy for the behaviour of calcium in a system, the relationship between the weathering rates and weathering patterns is lower than expected.

To further assess the relationship between lithology and modelled weathering rates, the total modelled weathering rates of the sites were also examined in relation to the weathering patterns from critical element ratios (Figure 5.9).

Figure 5.9 - Examining the relationships between total modelled weathering rates and weathering patterns derived from critical element ratios.
(Units are μeq m^{-2} yr^{-1} for weathering rates and % depletion of the Sr/Zr ratio between fresh and weathered rock samples for the weathering patterns)



The total modelled weathering rates show a stronger positive trend with the weathering patterns derived from critical element ratios (Figures 5.9) and resulted in a R^2 value of 0.569 (57%). Therefore, using the statistical strength of the relationship alone, strontium loss from rocks seems to provide a better proxy of the total weathering behaviour of the system.

In addition, I examined the relationship between simulated (modelled) decline in alkalinity and base saturation of the study sites and the weathering patterns derived from critical element ratios to further our understanding of the processes and timescale of water

quality decline (Figure 5.10 and 5.11).

Figure 5.10 - Examining the relationships between the modelled decline in alkalinity between 1856 and 1996 and weathering patterns derived from critical element ratios.

(Units are μeq l^{-1} for alkalinity concentrations and % depletion of the Sr/Zr ratio between fresh and weathered rock samples for the weathering patterns)

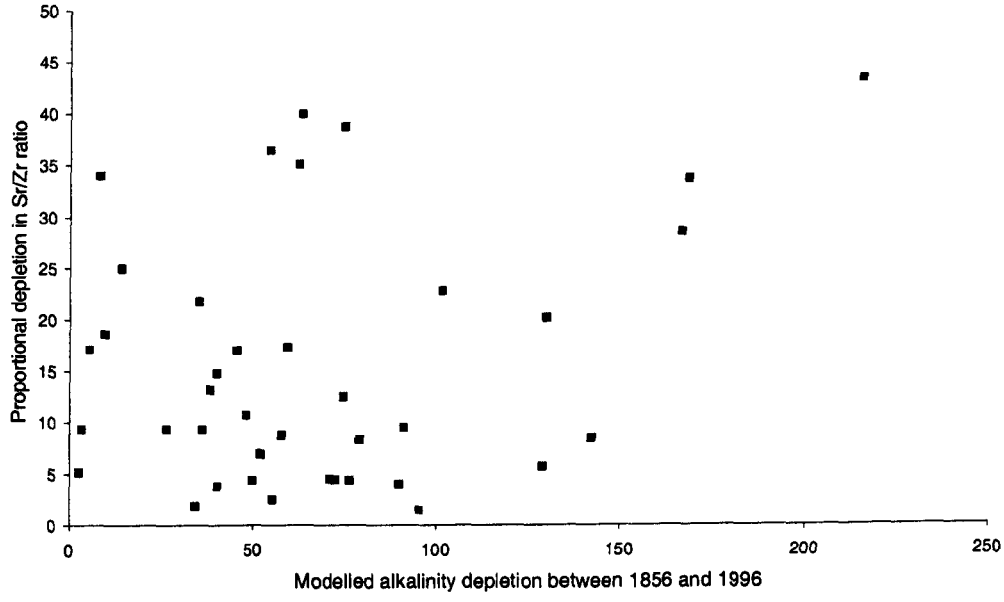
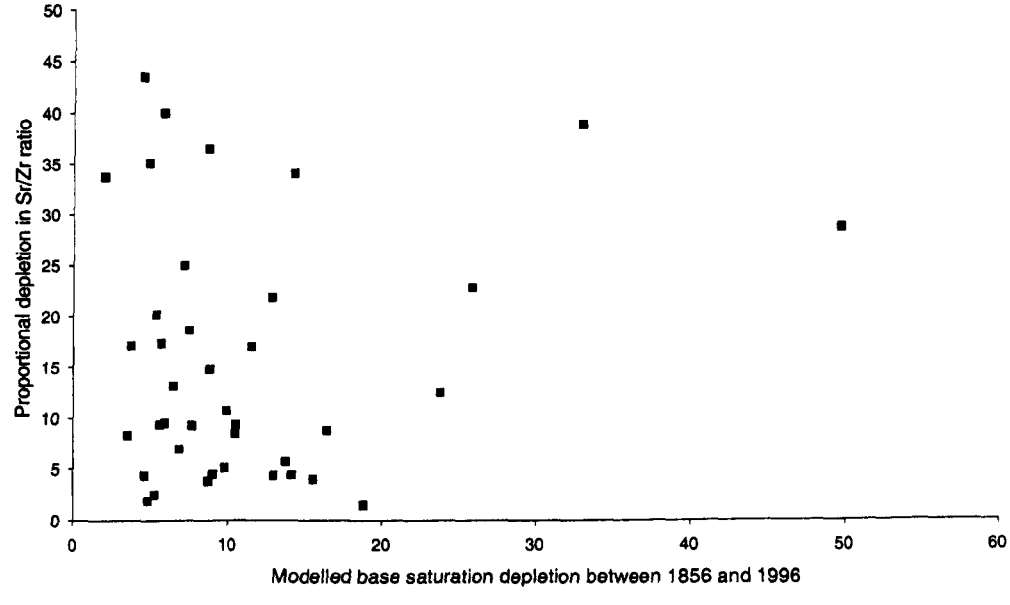


Figure 5.11 - Examining the relationships between the modelled decline in base saturation between 1856 and 1996 and weathering patterns derived from critical element ratios.

(Units are % of CEC for base saturation and % depletion of the Sr/Zr ratio between fresh and weathered rock samples for the weathering patterns)



The modelled decline of alkalinity (Figure 5.10) and base saturation (Figure 5.11) shows little correlation with the weathering patterns derived from critical element ratios, which suggests that you cannot simply link MAGIC generated declines in streamwater alkalinity and soil base saturation with the amount of strontium loss from the rocks. This is likely because the calculation of the weathering patterns takes no account of time period required for the Sr/Zr ratio depletion. Therefore, the rate of strontium depletion between the fresh and weathered fraction and hence the rate of weathering is unknown.

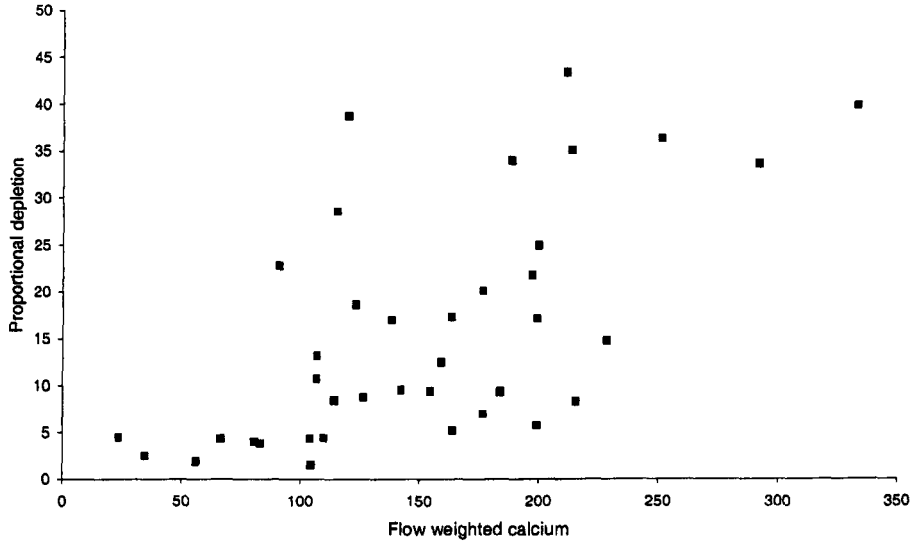
The hypothesis was that a fairly straightforward relationship existed between weathering patterns derived from critical element ratios (i.e. bedrock geology) and optimised weathering rates (Process-based modelling). This approach has been fairly successful because a reasonably strong relationship has resulted between the geological variables of rock chemistry weathering patterns and modelled weathering rates. However, the relationship found between the modelled decline in stream and soil chemistry and the weathering patterns derived from critical element ratios was relatively weak. This approach met with limited success because the rate of weathering could not be determined with data available. This may suggest that problems may be experienced if rock chemistry weathering patterns are used to predict streamwater chemistry on spatial and temporal scale. This hypothesis is fully explored in the next section (Section 5.4.2).

5.4.2. The links between rock chemistry and surfacewater chemistry

Modelled weathering rates have a significant relationship with weathering patterns derived from critical element ratios (Figure 5.9). However, this doesn't necessarily mean that rock chemistry weathering patterns are linked to surfacewater chemistry. This phase of the project's modelling aspect attempts to link rock chemistry weathering patterns in a predictable way to stream chemistry. The stream chemistry is widely variable across the study and this diversity may be due to the heterogeneous nature of the rock chemistry. The rock chemistry work (Section 3.3) and the water chemistry work (Section 4.3) are described previously in the thesis.

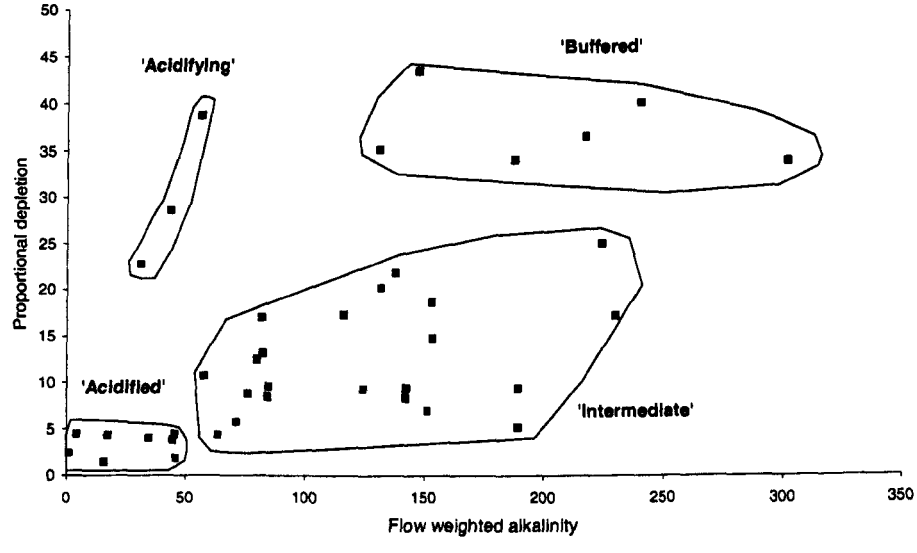
The streamwater calcium and alkalinity of the sites were examined in relation to the weathering patterns (Figure 5.12 and 5.13) to assess if a relationship exists between the lithology and streamwater chemistry. In addition, the modelled data were categorised into the five rock categories from Section 4.2.2 and compared to the streamwater calcium and alkalinity diagrams (Figure 5.14).

Figure 5.12 - Examining the relationships between streamwater calcium concentration and weathering patterns derived from critical element ratios. (Units are μeq l^{-1} for streamwater concentrations and % depletion of the Sr/Zr ratio between fresh and weathered rock samples for the weathering patterns)



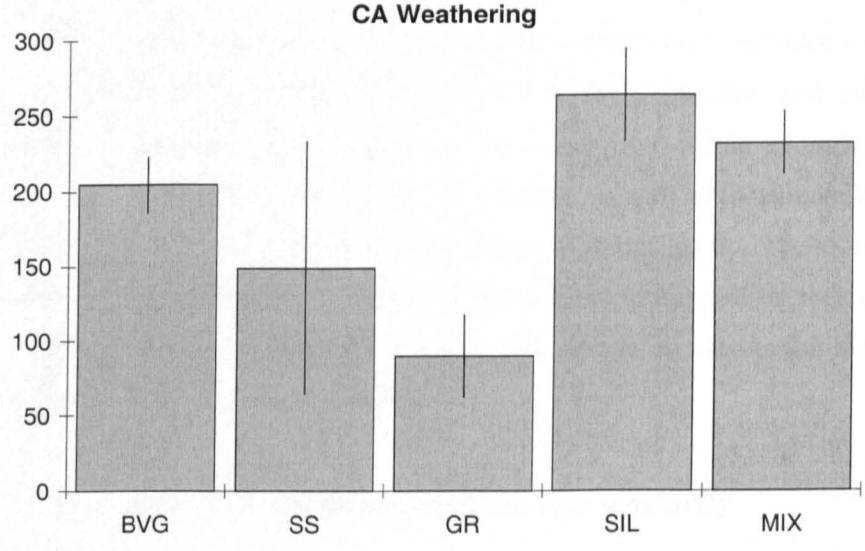
The streamwater calcium concentrations show a moderate positive trend with the weathering patterns derived from critical element ratios (Figure 5.12). The statistical strength of this relationship was tested by simple bivariate regression, which resulted in a R^2 value of 0.389 (39%).

Figure 5.13 - Examining the relationships between streamwater alkalinity concentrations and weathering patterns derived from critical element ratios. (Units are μeq l^{-1} for streamwater concentrations and % depletion of the Sr/Zr ratio between fresh and weathered rock samples for the weathering patterns)



The streamwater alkalinity concentrations also show a fairly weak positive trend with the weathering patterns derived from critical element ratios (Figures 5.13). A simple bivariate regression resulted in a R^2 value of 0.293 (29%). This relationship is slightly weaker than that found between the calcium concentrations and the weathering patterns (39%). The data plotted in Figure 5.13 can be apportioned to the following 'sensitivity' categories: (i) acidified; (ii) acidifying; (iii) intermediate; and (iv) buffered. These categories correspond well with the sensitive / less sensitive sites identified in Section 4.3.2. For example, all the sites in the 'acidified' group are located in very close proximity to each other and are underlain by the same resistant geology; the sites in the 'acidifying' group are located at very high altitude and receive the highest deposition load; and the sites in the 'buffered' group are located large distances from the sea at relatively low altitudes and receive low deposition loads.

Figure 5.14 - Mean modelled calcium weathering rates categorised by rock type
(Weathering units are μeq m^{-2} yr^{-1})



According to Figure 5.14, calcium weathering rates are high in Silurian Slate (265 μeq m^{-2} yr^{-1}) and mixed lithology catchments (232 μeq m^{-2} yr^{-1}), relatively high in Borrowdale Volcanic catchments (205 μeq m^{-2} yr^{-1}), and low in Skiddaw Slate (149 μeq m^{-2} yr^{-1}) and Granite catchments (90 μeq m^{-2} yr^{-1}). The large error bar on the Skiddaw Slate catchments is predominantly due to an extremely sensitive site (Liza Beck), which produced a modelled weathering rate of zero for calcium. Figure 5.14 shows that modelled calcium

weathering rates are related to dominant bedrock geology, although data was entered into MAGIC with no indication of the geology groupings.

5.4.3. Results of the integrative approach

The relationships between the weathering patterns and optimised weathering rates from MAGIC were examined to assess if a predictive link exists (Section 5.4.1), and this approach met with a fair degree of success (i.e. R^2 of 57%). The relationship between the weathering rates and weathering pattern would have been higher if it were not for two drawbacks with the approach. Firstly, bedrock samples demonstrate a wide variability of weathering capabilities between, and within, rock types. Secondly, MAGIC weathering rates do not represent an actual geological index, as they are essentially a fitted value based on the information that is entered into the model.

The relationship between weathering patterns and streamwater chemistry was examined to evaluate if a predictive link could be found (Section 5.4.2). This approach met with less success, with fairly low relationships (R^2 of 29 – 39%). The low relationships can be attributed to two inherent problems in the using this type of data to produce a predictive approach: 1) streamwater chemistry is the product of many complex and inter-related processes; and 2) the heterogeneous nature of rock chemistry within a catchment (and within rock types). For example, the weathering patterns, as well as the stream chemistry, display a large range of values within the Borrowdale Volcanic group. Therefore, a more accurate prediction of streamwater chemistry would require homogeneous rock chemistry within the catchment and this would allow a single rock sample (as used in this thesis) to be more representative of the catchment lithology.

5.5. Predictive model with special emphasis on acid sensitivity

In Section 5.2.2, we established the weaknesses of the various modelling approaches (i.e. process-based models are very data intensive whereas empirical models take no account of the processes involved). The new integrative approach has its roots in the complex processes of stream catchments, but its predictive element is purely empirical. The knowledge gained during the empirical, process-based and integrated modelling sections have provided potential ingredients for the new model, which should be able to predict water quality over space and time.

5.5.1 Potential 'ingredients' for the new model

During this thesis we have found the following: (a) a link between rock type and flow-weighted alkalinity (Section 4.3.2b); (b) a statistical link between S&N deposition, distance to sea and maximum altitude and flow-weighted alkalinity (Section 5.2.2b); (c) a link between MAGIC weathering rates and weathering patterns derived from critical element ratios (Section 5.4.1); and (d) a link between MAGIC weathering rates and rock type (Section 5.4.2). These findings have led us to the most likely candidates which will act as 'ingredients' for the new model – S&N deposition, distance to sea, maximum altitude and weathering patterns from critical element ratios. Distance to sea and maximum altitude are easy-to-measure variables which can provide data for the model even at sites with very limited information, and as long as spot samples of the catchment bedrock are collected the rock weathering patterns can be calculated. However, S&N deposition is relatively difficult to measure as a full spatial and temporal dataset requires a large network of rainwater collectors and dry deposition monitors, which are costly and difficult to implement.

Distance to the sea and maximum altitude are not dynamic variables, as they alter in space but not in time. Although the rock weathering patterns are not dynamic *per se*, the link with MAGIC weathering rates indicates that the data may be apportioned a rough annual catchment weathering rate if so desired. S&N deposition is the only truly dynamic variable as it represents the yearly amount of deposition received (ha^{-1} yr^{-1}) and thus can be altered to reflect temporal variation fairly easily. Therefore, S&N deposition, and possibly rock weathering patterns, are required if the model is to run dynamically (i.e. applicable on a temporal scale).

5.5.2 Developing and testing the new model on spatial and temporal scales

The development of the new model involved applying the stepwise regression method to flow-weighted alkalinity using the four independent variables selected as the best candidates for predictive modelling (Section 5.5.1). These variables account for approximately 70% of the variation (i.e. R^2 of 0.703) in the streamwater concentrations of alkalinity (Table 5.15).

Table 5.15 – Development of new model for alkalinity using stepwise regression analyses on 4 independent variables

Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Intercept	153.21	-		-
S&N Deposition (keq ha^{-1} yr^{-1})	-38.42	0.034		40.90
Distance to Sea (km)	3.03	< 0.001	**70.27**	20.68
Maximum Altitude (m)	-0.09	0.046		4.96
Rock Weathering (% depletion)	1.21	0.047		3.73

The most highly correlated variables to alkalinity are S&N deposition, which accounts for approximately 41% of the variation (p-value of 0.034), and distance to sea, which accounts for approximately 21% of the additional variation (p-value of < 0.001). Maximum altitude (p-value of 0.046) and rock weathering (p-value of 0.047) are less highly correlated with the stream's alkalinity, accounting for 5% and 4% of the addition explanation respectively.

Using the direction of the coefficients in Table 5.15 to infer the difference between low and high alkalinity sites results in a fairly sensible pattern. This approach suggests that high alkalinity sites have high rock weathering patterns, are located large distances from the sea (positive coefficients) at low maximum altitudes and receive low S&N deposition (negative coefficients). Or alternatively, low alkalinity sites have high maximum altitudes and S&N deposition, low rock weathering patterns and are located close to the sea.

Spatial applicability

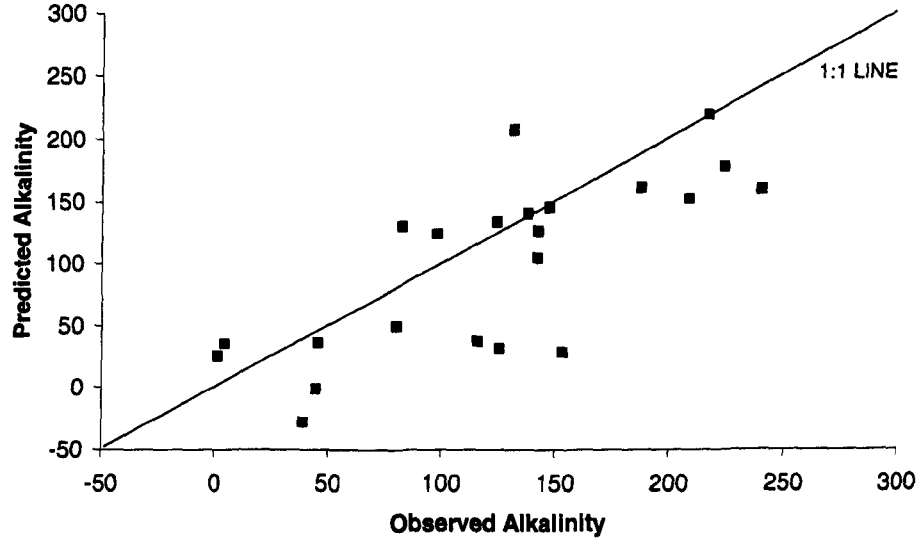
The spatial applicability of the simple predictive water quality model was tested using a regression model based on a subset of the data to predict alkalinity in the remaining subset (cf. method used in Section 5.2.2c). Using half the data, the stepwise regression method selected S&N deposition, distance to sea and maximum altitude as independent variables and accounts for approximately 73% of the variation in the alkalinity concentrations (Table 5.16). The regression model has selected three of the four variables from the model in Table 5.15 and has discarded the least highly correlated variable (rock weathering pattern).

Table 5.16 – Predicting alkalinity concentrations using a 50:50 split in the study data

Stepwise Predictors	Parameter Estimate	P value	R^2	Added explanation to total R^2 (%)
Intercept	96.33	-		-
S&N Deposition (keq ha^{-1} yr^{-1})	-24.93	0.022		42.40
Distance to Sea (km)	4.61	< 0.001	**73.08**	23.79
Maximum Altitude (m)	-0.11	0.046		6.79

The model used S&N deposition, distance to sea and maximum altitude to predict alkalinity concentrations and results in a reasonably close agreement between predicted and observed values as 17 of the 22 predicted values are within 50 μeq l^{-1} of the 1:1 line (Figure 5.15). The statistical strength of the three-variable model's predictive capabilities was a R^2 value of 0.559 (56%), which considering the complexity of the processes involved in streamwater chemistry is a fairly good approximation. Therefore using the three-variable model, it should be possible to predict alkalinity concentrations for the majority of Lake District streams within 50 μeq l^{-1}, as long as the streams to be tested possess the relevant catchment parameters within the range of the initial model. Although it was not tested here, it may also be possible to predict the alkalinity concentrations of streams outside the Lake District since the model does not include variables that are unique to the Lake District, such as the geology and soils.

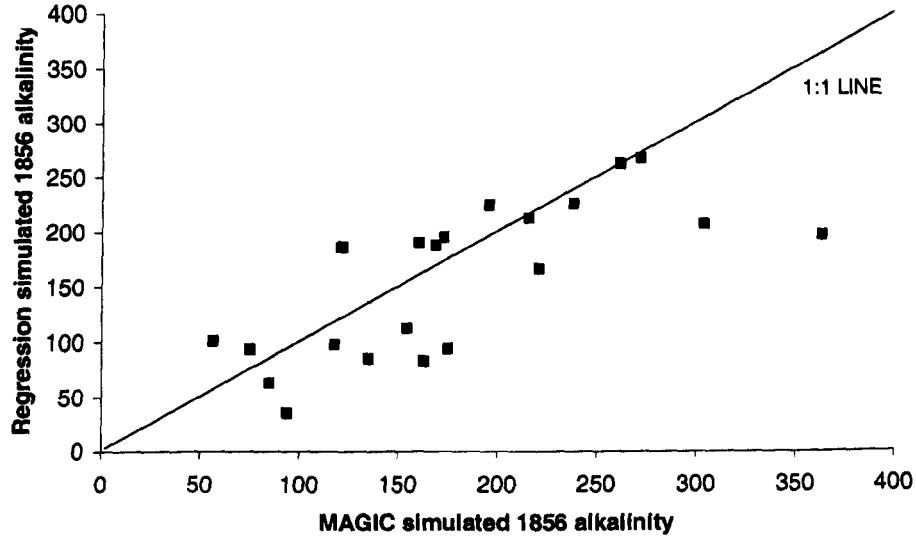
Figure 5.15 – Testing the spatial predictive capability of the new model. (Units: μeq l^{-1})



Temporal applicability

To reflect the trend of acid deposition over the last 140 years, the calibration procedure of MAGIC uses a scaling factor within the deposition sequence which has been estimated to take early industrial growth, "tall stacks" policies, peak emissions and emission curtailment into account (Appendix G). Here, to test the temporal applicability of the model, the alkalinity concentrations predicted for 1856 by MAGIC were compared with the results from the new model for the same year. The 'temporal' predictive water quality model used the same variables as the 'spatial' model in Table 5.16 (i.e. S&N deposition, distance to sea and maximum altitude) but S&N deposition was altered to 1856 levels by multiplying the present-day S&N deposition by the appropriate scaling factor from MAGIC. The statistical strength of the model's predictive capabilities was a R^2 value of 0.49 (49%), which considering the complexity of the processes involved in streamwater chemistry is a fairly good approximation. The alkalinity concentrations for 1856 using the two different methods are in a reasonably close agreement, with 17 of the 22 values within 50 $\mu eq\ l^{-1}$ of the 1:1 line (Figure 5.16).

Figure 5.16 – Testing the temporal predictive capability of the new model (Units: $\mu eq\ l^{-1}$)



Despite the closeness of the agreement between the two methods, care should be taken when interpreting the results and during the subsequent predictive modelling as we are assuming that the data produced by MAGIC is 'true' rather than the product of an

alternate model. However, assuming that the results from MAGIC are fairly accurate, it should be possible to predict alkalinity concentrations over a long timescale, both in the past and in the future, using this approach.

5.5.3 Implications of results for the hydrochemical modelling community

Models in the surface water quality field range from detailed catchment specific dynamic models like MAGIC (Cosby *et al.*, 1984) and SAFE (Warfvinge and Sverdrup, 1991) through to end-member modelling (Neal and Christophersen, 1989) and simple empirical relationships like the Henriksen nomograph (Henriksen, 1979, 1980). Although a process-based model is a powerful tool for prediction, it requires high-resolution catchment specific data to drive the model (e.g. cation exchange capacity, base saturation etc). Therefore, it is virtually impossible using nationally available datasets for geology, soils, land use and deposition to obtain accurate catchment data because of their low resolution. In contrast, an empirical model indicates relationships without giving any reasons as to how or why those relationships may have occurred and are usually based on a statistical relationship developed with a limited amount of information.

The overriding theme of this thesis has been to use easy-to-measure attributes to allow us to extrapolate to sites with little detailed information. Throughout the thesis, the underlying debate has been whether to use the 'best available data' or the 'simplest data'. It would have been possible to produce a model based upon a few intensively studied catchments but my aim was to produce a simple regional predictive model. Many studies have attempted to use catchment attributes for prediction purposes prior to this study with varying degrees of success. Examples of these studies include predicting alkalinity using geology (Lynch and Dise, 1985), predicting buffering capacity using runoff chemistry (Kirchner *et al.*, 1993), predicting acid sensitivity using geology and soil (Hornung *et al.*, 1990, 1995; Langan and Wilson, 1992), and predicting critical loads using geology, soil and deposition (Kernan, 1996). However, the majority of these studies use variables that are not easily exchangeable over time or space. Therefore, a considerable strength of this model is its spatial and temporal flexibility because the variables used in the final model are not unique to the Lake District or the 1990's.

An assessment of the models efficiency must conclude that it provides a fairly good approximation of alkalinity concentrations on a spatial (R^2 value of 56%) and temporal scale (R^2 value of 49%), as the predicted alkalinity was within 50 $\mu eq\ l^{-1}$ of the observed

(simulated) values at 77% of the sites. However, the acid test of the model's spatial and temporal applicability would be the prediction of alkalinity concentrations in streams outside the Lake District and into the future with a high degree of accuracy. This prospective research will hopefully take place after the completion of this project.

5.6. Summary of Chapter

During this chapter, the water, rock and catchment characteristic data of the stream catchments were subjected to several statistical exercises. The primary aim of this chapter was to highlight the important catchment factors governing streamwater alkalinity, thus allowing a simple predictive water quality model to be created.

Initially, the water and catchment characteristic data were subjected to stepwise multiple regression analyses, where S&N deposition, distance to sea and maximum altitude provided a high R^2 value for alkalinity (0.656). The predictive capability of this model was tested using one half of the data for model development and the other half for prediction. This resulted in reasonably close agreement between predicted and observed values as most of the predicted values are within 50 $\mu eq\ l^{-1}$ of the 1:1 line and a R^2 value of 0.559 (56%).

The water and catchment characteristic data were then subjected to principal component analyses. It was found that Silurian Slates, forestry, agriculture and thick soil were associated with sites that are less sensitive to acidification (i.e. high alkalinity sites), whereas Borrowdale Volcanics, upland vegetation, maximum altitude, high S&N deposition and high annual runoff and rainfall were associated with sites highly sensitive to acidification (i.e. low alkalinity sites). Four variables with the highest PCA coefficients (Silurian Slates, S&N deposition, annual runoff and annual rainfall) were entered into a regression model to test the predictive capability of the 'model'. The predictions produced were comparable with the stepwise regression models (relationship with alkalinity – R^2 of 35%). This method therefore provided a potentially useful way of integrating several intercorrelated catchment parameters with streamwater chemistry.

The catchments were modelled with the process-based model, MAGIC, to ascertain the weathering rates of the individual catchments. The MAGIC weathering rates were then related to the weathering patterns derived from critical element ratios (Section 3.5.3) using a bivariate regression. There was a fairly strong link between the two variables (R^2 of 57%), which suggested that it might be possible to predict the weathering rate of a catchment simply by collecting a single rock sample.

The simple predictive water quality model created in Section 5.5 provided a fairly good approximation of alkalinity concentrations on a spatial (R^2 value of 56%) and temporal scale (R^2 value of 49%). The predicted alkalinity was within 50 $\mu eq\ l^{-1}$ of the observed (simulated) values at 77% of the sites.

In summary, the model has a fairly good predictive capability, but its spatial and temporal applicability outside the study area is an unknown quantity. The model needs to predict alkalinity with a high degree of accuracy in a variety of study areas to be of use to policy makers and the hydrological community. This has not been tested as yet, however, the variables used in the final model are not unique to the Lake District or the 1990's thus such an approach may prove to be an extremely useful tool indeed.

CHAPTER 6

Conclusions

"It is a good morning exercise for a research scientist to discard a pet hypothesis every day before breakfast. It keeps him young." – Konrad Lorenz

"Research is the process of going up alleys to see if they are blind." – Marston Bates

"Basic research is what I am doing when I don't know what I am doing." – Werner von Braun

"The most exciting phrase to hear in science (the one that heralds new discoveries) is not Eureka but That's funny...." – Isaac Asimov

6.1. Introduction

This thesis has examined the various controls on streamwater chemistry in the Lake District with the specific aim of creating a predictive regional water quality model. This chapter summarizes the results presented in earlier chapters (Section 6.2), identifies the sources of uncertainty in the study data (Section 6.3), addresses the weaknesses of the research (Section 6.4) and postulates some areas for future research (Section 6.5).

6.2. Summary of thesis results

The research undertaken during this thesis took place in three discrete stages: (i) Examining the chemistry of bedrock samples (Section 6.2.1); (ii) Examining the chemistry of streamwater samples (Section 6.2.2); and (iii) Using the catchment characteristics and geochemical data to create a predictive water quality model (section 6.2.3)

6.2.1 Whole-rock chemistry

The rock samples in this study were classified as andesite (n=21), dacite (n=14), greywacke (n=7), lithic arenite (n=5), metamorphosed mudstone (n=3) and granite (n=1). Examination of the rocks using variation diagrams suggested that the rock samples were very variable within, as well as between, the geological groups. The most heterogeneous geological group was the Borrowdale Volcanic Group, which displayed the largest range in element compositions. This heterogeneity is most likely due to the different amounts of fractionation that occurs within the Borrowdale Volcanic rocks (cf. Rollinson, 1993). The

Silurian Slates rock samples were apportioned to two discrete sub-groups, which are probably due to differing weathering conditions and is most likely explained by the mineralogical maturity hypothesis (cf. Bhatia, 1983).

The majority of the elements exhibited fairly conservative behaviour between fresh and weathered fractions. Calcium and strontium exhibited the most prominent depletion patterns and lead demonstrated the most prominent enrichment pattern. The strontium-zirconium ratio was used derive weathering patterns. The Borrowdale Volcanic Group exhibited the most heterogeneous strontium weathering patterns (some weathered while others didn't), whereas very little weathering occurred in the Skiddaw Slate samples.

6.2.2 Major-ion chemistry

The sensitivity of Lake District streams to acidification was assessed using streamwater calcium and alkalinity as indicators. Using the 200 $\mu eq\ l^{-1}$ threshold of sensitivity, 69 (calcium) to 75% (alkalinity) of the study streams were considered sensitive to acidification. Alkalinity and base cation concentrations were low in Borrowdale Volcanic, Skiddaw Slate and granite catchments. Using the other catchment characteristic patterns, we inferred that this is most likely due to: (a) low base cation resupply via weathering of the bedrock, (b) short residence times in thin soils, (c) longer residence times in thick, acidic soils, and/or (d) inputs of anions from acid precipitation. In contrast, alkalinity and base cation concentrations were high in Silurian Slate, mixed lithology and agricultural catchments. The catchment characteristic patterns helped us to infer that (a) easily-weathered bedrock provides a higher base cation supply, (b) thick soils have high residence times and more capacity for cation exchange, and/or (c) agriculture and liming create an additional source of base cations.

A reduction in catchment buffering, perhaps as a consequence of chronic acid deposition, may have caused Lake District streamwater quality to decline significantly since the early 1970s. Any future increase in acid deposition (or conversion to agriculture) would have severe implications for the chemistry of Lake District streams.

6.2.3 Model development and evaluation

It was a matter of debate whether to use the 'best available data' or the 'simplest data'. However, the prevailing argument of this thesis was to use easy-to-measure attributes, which makes it easier to extrapolate to sites with little detailed information.

The multiple regression model for alkalinity explained 66% of the variation using three variables and predicted alkalinity concentrations with a high degree of accuracy. In addition, four intercorrelated catchment parameters identified by principal component analysis predicted alkalinity concentrations with a similar degree of accuracy. Furthermore, weathering rates derived from MAGIC had a strong link with weathering patterns derived from critical element ratios.

During this thesis we have found: (a) a pattern between rock type and flow-weighted alkalinity (Section 4.3.2b); (b) a statistical link between S&N deposition, distance to sea and maximum altitude and flow-weighted alkalinity (Section 5.2.2b); (c) a link between MAGIC weathering rates and weathering patterns derived from critical element ratios (Section 5.4.1); and (d) a link between MAGIC weathering rates and rock type (Section 5.4.2). These findings led us to 'ingredients' for a new empirical model.

The spatial applicability of the model was tested by predicting the alkalinity concentrations in a subset of the data. This approach predicted alkalinity concentrations with a degree of accuracy of $\pm$ 50 μeq l^{-1}. Using this model, it should be possible to predict alkalinity concentrations for Lake District streams to this level of accuracy, as long as the streams to be tested possess the relevant catchment parameters within the range of the initial model.

The temporal applicability of the model was tested by predicting 1856 alkalinity concentrations. This approach predicted alkalinity concentrations with a degree of accuracy of $\pm$ 50 μeq l^{-1} when compared with 1856 alkalinity from MAGIC. However, care should be taken when interpreting the results, as close agreement doesn't necessarily equate to legitimacy. That is, the data produced by MAGIC is only the product of an alternate model and not actual 1856 chemistry data. It should be possible to predict alkalinity concentrations over a long timescale, both in the past and in the future, using this approach assuming that the MAGIC results are fairly accurate.

The model's spatial and temporal flexibility is one of its considerable strengths as the variables used in the final model are not unique to the Lake District or the 1990's. Therefore, as long as the streams possess the relevant catchment parameters within the range of the initial model, one should be able to predict alkalinity concentrations with a high degree of accuracy in a variety of study areas. Although this model is not as powerful as a process-based model, its low data requirements means that it can be applied with a limited amount of information and thus may prove to be an extremely useful tool indeed.

6.3. Sources of uncertainty

There were several sources of uncertainty with the data used during this thesis. The following sub-sections discuss the limitations of the geology (Section 6.3.1); soils (Section 6.3.2), land use (Section 6.3.3) and atmospheric deposition (Section 6.3.4).

6.3.1. Solid geology

The 1:250,000 solid geology map for the Lake District is only a 'broad' indication of the underlying lithology. For example, it does not show local surficial deposits (such as till and alluvium) resulting from recent Pleistocene glaciations and it uses abridged geological groups (so small geological groups found on higher resolution maps are lost). In addition, the physical classification (i.e. rock types divided into sedimentary, metamorphic and igneous classes) used by British Geological Survey may have little bearing on whether a rock group is lithologically and/or geochemically homogeneous.

6.3.2. Soils

The Hydrology of Soil Types (HOST) classification (Boorman *et al.*, 1995) was used as the soil variable in this study. The classification was derived from Soil Survey maps (Avery, 1980) and is therefore the most detailed regional information available.

6.3.3. Land Use

The Land Cover map records 25 cover types as dominant land cover in a 1km x 1km grid square. Since the land cover data only indicates the dominant land cover class in 1km^2 it may not accurately represent land cover diversity below 1km^2 resolution. Since the size of the study catchments ranges between 0.3 and 11.7 km^2, the data derived from the map may not be entirely accurate.

6.3.4. Atmospheric deposition

The atmospheric deposition component of the study used 20km x 20km grids of precipitation-weighted annual mean ion fluxes, which are calculated using the geostatistical technique of kriging. However, actual atmospheric deposition may vary by large amounts over a 20km by 20km grid square due to variations in factors such as altitude differences, land use and proximity to the sea. Therefore, data at this resolution should be used

extremely cautiously when attempting to identify deposition at the catchment scale. This was the primary reason for employing the Cl balance method for catchment-scale atmospheric deposition, as this approach is more likely to reflect individual catchment characteristics (e.g. altitude differences and sea-salt influences) than the 20 by 20km grid deposition estimates.

6.4. Weaknesses of research

There are several weaknesses and limitations with the research methods utilised in this thesis. These need to be taken on board so that the findings of this research are interpreted correctly.

1. Most of the study sites were underlain by Borrowdale Volcanic bedrock. This may well have resulted in geology variables being excluded from the statistical procedures despite being important factors in determining streamwater alkalinity. This fact was probably compounded by the fact that the Borrowdale Volcanic group is chemically and physically complex. Streams draining this group have a wide range of solute concentrations due to bedrock heterogeneity and thus statistically significant relationships are unlikely.
2. Low sampling frequency. Ideally, we would have sampled on a daily basis to achieve a full temporal picture of Lake District streamwater chemistry, but the nature of Ph.D. research meant that when the sampling strategy was devised, time and money were paramount considerations. However, time and money considerations would also be at the forefront in the situations where such results would be applied.
3. Low resolution deposition data. The atmospheric deposition component in the model (S&N deposition) was calculated using actual rainfall measurements from one monitoring site by assuming chloride is conservative. However, the nature of the Cl balance method means that it is entirely possible that any errors in the original data will have been magnified during recalculation (Rowntree, 1981; Cohen, 1988).
4. Problems with percentages. They don't give a true picture of what is going on. For example, 1% limestone in a large catchment represents more catchment area and therefore may be more influential in determining streamwater chemistry than in a small catchment. Likewise, percentages take no account of the geographic position, 1% limestone will be more influential if the stream passes

over it, rather than it be located somewhere where it doesn't even effect the stream.

5. Weaknesses in the statistical approach (1). It is impossible to assess the cause and effect of the catchment processes due to the assumptions and limitations of the statistical methods. For example, variables strongly associated with each other may both be controlled by a third factor.
6. Weaknesses in the statistical approach (2). Splitting the data in half for predictions only shows the strength of the database. Ideally, the model needs to be based on samples taken from one area and applied to another (unsampled) area. Samples collected from this area are used to validate the model predictions. This method is more scientifically robust than the '*post hoc*' hypothesis testing utilised by this study.
7. Weaknesses in the statistical approach (3). Given the known assumptions and limitations of the two statistical methods employed, some consideration should have been given to canonical correspondence analysis. CCA has all the strengths of multiple regression and PCA but has fewer assumptions and limitations, and thus may have given rise to more significant results.

6.5. Further research

There are two main areas that might be considered fruitful areas of further research. Firstly, there is considerable scope for improving the model predictions by improving data input. More frequent sampling and the widespread availability of accurate deposition data would significantly improve the model's accuracy. Secondly, the model could be utilised for predicting the alkalinity of streams on a spatial and temporal scale.

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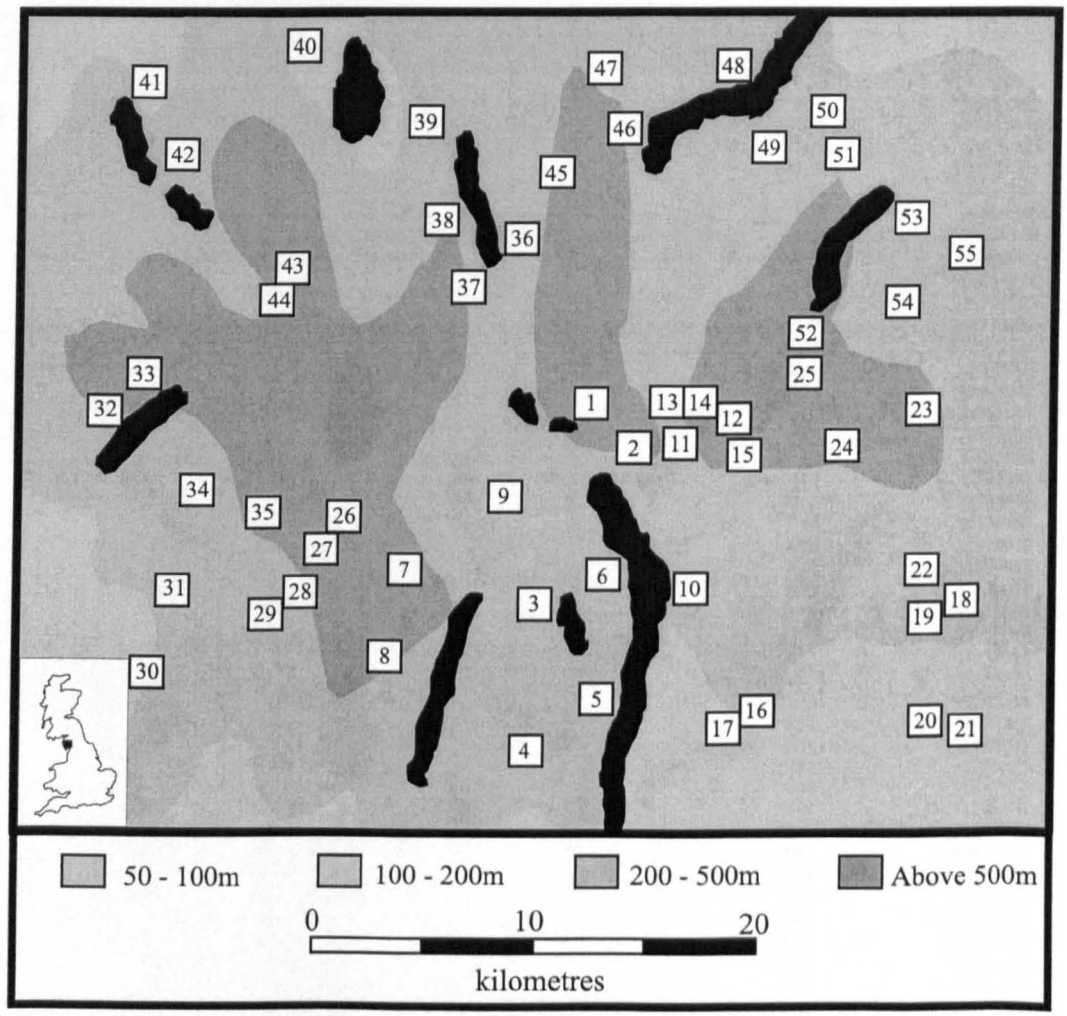
APPENDIX A

Sample Locations

A.1 Stream Study

By manually overlaying an Ordnance Survey map on top of the solid geology map of the Lake District, approximately 100 streams were chosen on the basis of the geological range deemed to fall within the river's catchment area. For the purpose of this study, the original 100 sites were reduced to 55 after a field reconnaissance exercise was carried out in March 1996.

Figure A1 - Location of the 55 stream survey sites (also showing relief)



A.1.1 Site Locations

Locations of the streams are shown in Figure A1. Water samples were collected at each site on a bimonthly basis for one year (6 surveys in all). The sample sites were all small headwater streams to minimise noise in the chemical signal from other influences to those considered in the study (i.e. sewage outfalls, road salting etc.) and to get the simplest relationships with geology and other environmental factors. Details of sampling strategy and analytical methods are fully discussed in Chapter 2 and Appendix B. The name of each stream, catchment area and its Ordnance Survey grid reference are given in Table A1.

Table A1 - Details of the 55 stream sites used in the study

Site No.	Name of stream	Area (km^2)	Grid reference
1	Rydal Beck	7.68	33665068
2	Stock Ghyll	5.45	33915055
3	How Beck	0.52	33494975
4	Dale Park Beck	4.35	33494918
5	Low Cunsey Beck	0.91	33784931
6	Belle Grange Beck	0.84	33874992
7	Red Dell Beck	1.66	32894988
8	Torver Beck	8.16	32864951
9	Washfall Beck	0.44	33325026
10	Mill Beck 1	2.87	34224982
11	Stony Beck	0.59	34155043
12	Hagg Gill	3.19	34235055
13	Trout Beck	5.57	34175064
14	Woundale Beck	2.85	34175063
15	Hall Gill	1.29	34505043
16	Chapel Beck	8.26	34624928
17	Tributary of Chapel Beck	1.03	34594926
18	Grayrigg Hall Beck	2.81	35834976
19	Flodder Beck	0.84	35714957
20	St Sundays Beck	2.46	45714923
21	Killington Reservoir Trib.	0.79	35934933
22	Tributary of River Mint	0.30	35575001
23	Borrow Beck	7.08	35495042
24	Bannisdale Beck	2.05	35155044
25	River Sprint	5.42	34805071
26	Moasdale Beck	3.43	32465018
27	Castle How Beck	0.62	32365003
28	Tarn Beck	10.78	32324969
29	Sling Beck	1.16	32134955
30	Holehouse Gill	4.39	31814933
31	Crosby Gill	6.12	31874953
32	Greendale Gill	2.89	31435057
33	Nether Beck	6.62	31615067
34	Whillan Beck	11.73	31785016
35	Hardknott Gill	1.63	32155011
36	Whelpside Gill	1.84	33255137
37	Wyth Burn	5.75	33195125
38	Launchy Ghyll	2.75	33095158
39	Shoulthwaite Gill	3.54	32985203
40	Coledale Beck	6.42	32285235
41	Liza Beck	4.00	31615211
42	Mill Beck 2	4.91	31795174
43	Sour Milk Gill	1.79	32335122
44	Styhead Gill	7.05	32355116
45	Glenridding Beck	5.68	33625173
46	Glencoyne Beck	2.91	33825187
47	Aira Beck	5.01	33685209
48	Parkhouse Gill	1.51	34265208
49	Fusedale Beck	3.37	34455187
50	Heltondale Beck	5.23	34875198
51	Cawdale Beck	5.57	34945179
52	Gatescarth Beck	0.60	34695107
53	Naddle Beck	2.85	35095151
54	Mosedale Beck	10.99	35045120
55	Tailbert Gill	0.51	35345142

A.2 Rock Study

In addition to collecting water samples at the 55 sample sites in the survey (Table A1) rock samples were collected from the predominant geological type of each catchment. One rock sample was collected from exposed outcrops upstream of the stream sample at each site.

A.2.1 Site Locations

Sample locations for the rocks are shown in Figure A2. Rock samples were collected from 52 of the stream sites. No rock sample was collected at Flodder Beck (19), Crosby Gill (31) or Parkhouse Gill (48) due to the lack of outcrops. Details of the sampling strategy and the analytical methods are fully discussed in Chapter 2 and Appendix B.

Figure A2 - Location of the 52 rock sample sites (also showing solid geology)

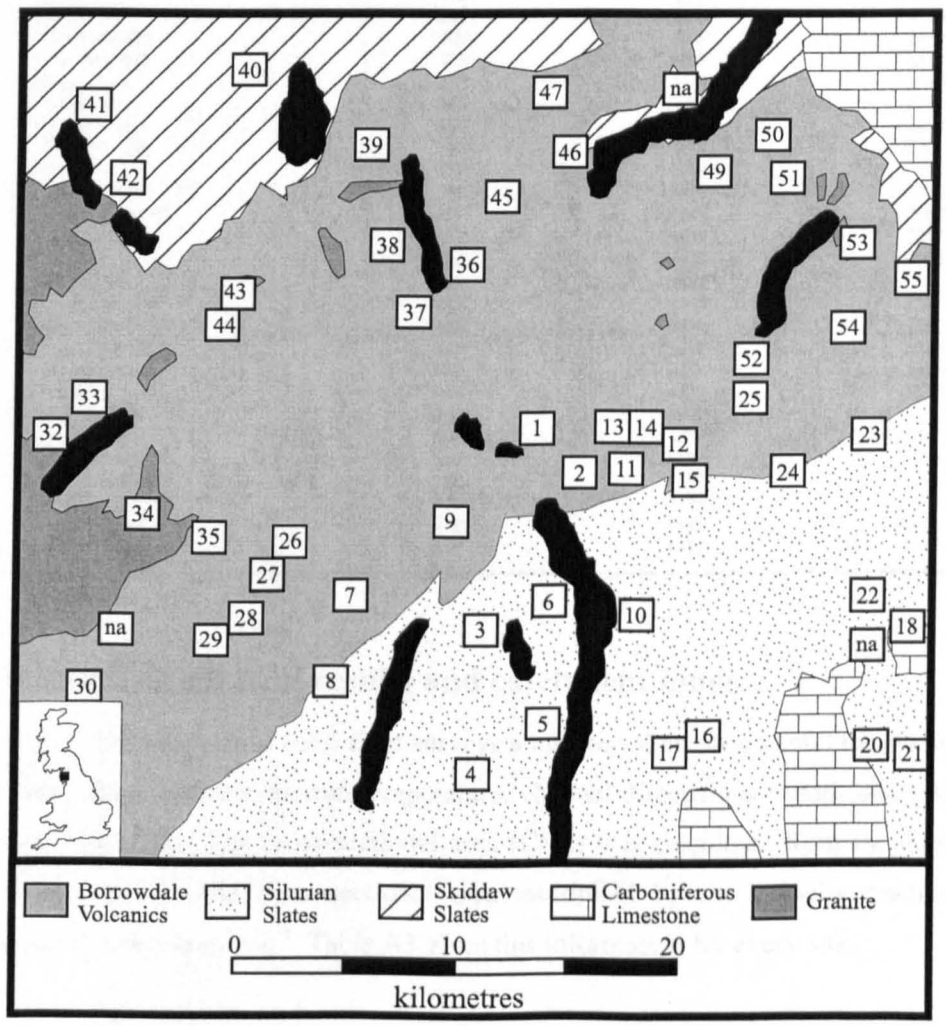


Table A2 – Details of the rock samples used in the study

Name of stream	Sample No. (fresh)	Sample No. (weathered)	Grid reference
Rydal Beck	1F	1W	366068
Stock Ghyll	2F	2W	391054
How Beck	3F	3W	349975
Dale Park Beck	4F	4W	348925
Low Cunsey Beck	5F	5W	378931
Belle Grange Beck	6F	6W	387992
Red Dell Beck	7F	7W	289988
Torver Beck	8F	8W	286951
Washfall Beck	9F	9W	332026
Mill Beck 1	10F	10W	422982
Stony Beck	11F	11W	415043
Hagg Gill	12F	12W	423055
Trout Beck	13F	13W	417064
Woundale Beck	14F	14W	417063
Hall Gill	15F	15W	450043
Chapel Beck	16F	16W	462930
Tributary of Chapel Beck	17F	17W	459926
Grayrigg Hall Beck	18F	18W	583976
St Sundays Beck	20F	20W	571923
Killington Reservoir Trib.	21F	21W	593933
Tributary of River Mint	22F	22W	558001
Borrow Beck	23F	23W	549042
Bannisdale Beck	24F	24W	515044
River Sprint	25F	25W	480071
Moasdale Beck	26F	26W	246018
Castle How Beck	27F	27W	236003
Tarn Beck	28F	28W	230965
Sling Beck	29F	29W	213955
Holehouse Gill	30F	30W	181933
Greendale Gill	32F	32W	143059
Nether Beck	33F	33W	161067
Whillan Beck	34F	34W	178016
Hardknott Gill	35F	35W	215011
Whelpside Gill	36F	36W	326137
Wyth Burn	37F	37W	315125
Launchy Ghyll	38F	38W	309158
Shoulthwaite Gill	39F	39W	298203
Coledale Beck	40F	40W	226235
Liza Beck	41F	41W	163210
Mill Beck 2	42F	42W	180174
Sour Milk Gill	43F	43W	232122
Styhead Gill	44F	44W	235116
Glenridding Beck	45F	45W	362173
Glencoyne Beck	46F	46W	382187
Aira Beck	47F	47W	365210
Fusedale Beck	49F	49W	445184
Heltondale Beck	50F	50W	486199
Cawdale Beck	51F	51W	495179
Gatescarth Beck	52F	52W	469106
Naddle Beck	53F	53W	509150
Mosedale Beck	54F	54W	504118
Tailbert Gill	55F	55W	535141

A.3 Individual field results and catchment maps

During each of the 6 field surveys a number of environmental factors were recorded - date, time, weather, stream temperature, channel dimensions (width and interval depths) and streamflow. The cross-sectional area (CSA) was calculated from the depth and width measurements. The cross-sectional area multiplied by the velocity readings gives the discharge (Q) in $m^3 sec^{-1}$. Table A3 gives this information for every site.

Table A3 – Survey details for each site

Site Name	Date	Time	Weather	Width (m)	CSA (m^2)	Q ($m^3 sec^{-1}$)	Temp (°C)
Rydal Beck	30/04/96	9.30	OVERCAST	3.86	0.085	3.38	4.2
	16/07/96	9.00	SUNNY	3.91	0.102	1.64	7.6
	10/09/96	9.15	OVERCAST	3.96	0.099	1.88	12.3
	11/11/96	9.00	OVERCAST	4.93	0.151	10.13	3.2
	13/01/97	9.00	OVERCAST	4.76	0.112	5.46	4.2
	10/03/97	8.50	OVERCAST	4.72	0.127	7.56	4.2
Stock Ghyll	30/04/96	10.30	OVERCAST	5.13	0.100	4.81	5.6
	16/07/96	9.40	SUNNY	4.67	0.051	0.29	8.7
	10/09/96	9.55	OVERCAST	4.44	0.036	0.72	11.3
	11/11/96	9.45	OVERCAST	5.27	0.085	6.33	3.3
	13/01/97	9.40	OVERCAST	5.32	0.090	5.59	4.6
	10/03/97	9.30	SUNNY	5.37	0.079	4.90	4.6
How Beck	30/04/96	11.15	OVERCAST	1.32	0.010	0.75	7.5
	16/07/96	10.20	SUNNY	1.28	0.004	0.36	8
	10/09/96	10.35	BRIGHT	1.22	0.003	0.31	12.1
	11/11/96	10.25	OVERCAST	1.06	0.011	0.33	5.5
	13/01/97	10.20	OVERCAST	1.36	0.008	0.72	4.9
	10/03/97	10.20	OVERCAST	1.18	0.007	0.35	4.8
Dale Park Beck	30/04/96	12.00	DRIZZLE	3.53	0.052	2.47	7.9
	16/07/96	10.50	SUNNY	3.48	0.024	0.25	8.5
	10/09/96	10.55	BRIGHT	3.16	0.016	0.24	10.7
	11/11/96	10.50	BRIGHT	3.22	0.048	3.09	5.7
	13/01/97	10.40	OVERCAST	3.36	0.035	1.08	5.2
	10/03/97	10.50	OVERCAST	3.19	0.052	1.09	4.9
Low Cunsey Beck	30/04/96	12.45	RAIN	2.32	0.019	0.69	7.1
	16/07/96	11.15	SUNNY	1.97	0.009	0.31	7.1
	10/09/96	11.15	OVERCAST	1.99	0.004	0.30	11.4
	11/11/96	11.20	BRIGHT	2.59	0.020	1.19	5.8
	13/01/97	11.00	OVERCAST	1.8	0.013	0.65	5.4
	10/03/97	11.30	SUNNY	1.84	0.018	0.56	5.4
Belle Grange Beck	30/04/96	14.30	RAIN	2.1	0.025	0.55	6.5
	16/07/96	11.45	SUNNY	1.56	0.006	0.29	7.9
	10/09/96	11.40	OVERCAST	1.42	0.005	0.25	11.8
	11/11/96	11.55	BRIGHT	1.84	0.026	0.66	4.2
	13/01/97	11.25	OVERCAST	1.79	0.020	0.39	5.7
	10/03/97	12.00	SUNNY	1.74	0.019	0.21	6.1
Red Dell Beck	30/04/96	15.20	OVERCAST	2.56	0.051	3.35	6
	16/07/96	12.30	SUNNY	2.74	0.042	4.80	10.3
	10/09/96	12.15	BRIGHT	2.52	0.026	2.73	12.6
	11/11/96	13.00	BRIGHT	2.59	0.045	3.58	4.3
	13/01/97	12.00	OVERCAST	2.03	0.032	2.24	4.1
	10/03/97	12.45	SUNNY	2.16	0.045	2.61	5.2
Torver Beck	30/04/96	16.20	OVERCAST	4.3	0.074	11.28	7.5
	16/07/96	13.15	SUNNY	4.25	0.056	5.22	9.7
	10/09/96	12.50	BRIGHT	4.16	0.053	3.86	11.7
	11/11/96	14.00	OVERCAST	4.31	0.156	12.51	4.3
	13/01/97	12.45	OVERCAST	4	0.153	10.26	4.2
	10/03/97	13.40	SUNNY	3.94	0.143	9.36	4.8
Washfall Beck	30/04/96	17.40	DRIZZLE	1.18	0.030	0.83	7.2
	16/07/96	14.30	SUNNY	0.98	0.012	0.22	7.2
	10/09/96	13.30	OVERCAST	0.78	0.005	0.09	11.2
	11/11/96	14.35	OVERCAST	1.09	0.016	0.64	5.8
	13/01/97	13.20	OVERCAST	0.97	0.020	0.64	4.5
	10/03/97	14.20	SUNNY	1.02	0.018	0.51	5.2

Table A3 (contd.) – Survey details for each site

Site Name	Date	Time	Weather	Width (m)	CSA (m^2)	Q ($m^{-3}sec^{-1}$)	Temp (°C)
Mill Beck 1	01/05/96	9.25	OVERCAST	2.72	0.033	3.38	8.3
	17/07/96	9.10	SUNNY	2.56	0.015	0.69	4.4
	10/09/96	14.30	OVERCAST	2.37	0.012	0.58	12.9
	12/11/96	10.25	SUNNY	4.28	0.057	3.06	6.8
	14/01/97	10.15	SUNNY	3.25	0.032	0.61	6.9
	10/03/97	15.10	SUNNY	3.31	0.035	0.77	5.9
Stony Beck	01/05/96	10.20	OVERCAST	2.56	0.050	1.65	6.7
	16/07/96	16.20	SUNNY	2.06	0.015	0.46	9.3
	11/09/96	10.15	OVERCAST	1.92	0.013	0.23	11.4
	11/11/96	15.20	RAIN	2.25	0.022	0.54	5.6
	13/01/97	13.55	OVERCAST	2.07	0.034	0.75	4.4
	11/03/97	9.50	SUNNY	2.12	0.027	0.69	4.8
Hagg Gill	01/05/96	11.15	OVERCAST	2.54	0.051	3.73	8
	16/07/96	16.50	SUNNY	2.46	0.035	1.65	11.9
	11/09/96	10.35	OVERCAST	2.14	0.036	2.14	10.9
	11/11/96	15.40	RAIN	2.86	0.063	7.04	5.4
	13/01/97	14.10	OVERCAST	2.36	0.045	4.13	4.3
	11/03/97	10.15	SUNNY	2.29	0.046	4.97	4.9
Trout Beck	01/05/96	12.30	RAIN	4.75	0.215	10.41	6.3
	16/07/96	15.30	SUNNY	4.62	0.203	10.16	11.8
	11/09/96	9.40	OVERCAST	3.96	0.097	4.02	11.3
	12/11/96	9.20	FAIR	5.37	0.214	27.14	4.1
	14/01/97	9.20	SUNNY	3.1	0.123	8.23	4.3
	11/03/97	8.55	SUNNY	3.06	0.122	8.11	3.6
Woundale Beck	01/05/96	13.00	RAIN	4.17	0.164	2.05	7.2
	16/07/96	16.00	SUNNY	4.02	0.150	1.83	8.7
	11/09/96	9.55	OVERCAST	4.06	0.099	1.59	11.5
	12/11/96	9.50	FAIR	3.99	0.062	8.69	4.2
	14/01/97	9.35	SUNNY	2.53	0.082	2.81	4.5
	11/03/97	9.20	SUNNY	2.42	0.076	2.56	4
Hall Gill	01/05/96	15.20	DRIZZLE	3.58	0.062	2.12	7.7
	17/07/96	10.00	SUNNY	1.84	0.014	0.14	4.6
	11/09/96	11.25	OVERCAST	1.76	0.014	0.13	11.2
	12/11/96	10.55	FAIR	4.56	0.038	2.38	4.6
	14/01/97	10.55	SUNNY	2.09	0.027	0.39	4.8
	11/03/97	11.15	SUNNY	2.15	0.037	0.49	5.7
Chapel Beck	01/05/96	17.00	DRIZZLE	3.7	0.063	9.31	8.6
	20/07/96	16.55	SUNNY	2.5	0.018	0.99	7.5
	11/09/96	15.25	RAIN	2.46	0.016	0.92	12.3
	12/11/96	15.15	OVERCAST	3.76	0.062	12.15	5.1
	14/01/97	14.20	SUNNY	2.86	0.031	3.04	5.2
	11/03/97	15.15	SUNNY	2.96	0.034	2.99	7.1
Chapel Beck Trib	01/05/96	17.30	OVERCAST	1.26	0.022	0.71	8.7
	20/07/96	16.40	SUNNY	0.96	0.010	0.09	8.6
	11/09/96	15.50	RAIN	0.74	0.007	0.06	12.1
	12/11/96	15.50	OVERCAST	1.39	0.020	1.10	5.2
	14/01/97	14.35	SUNNY	1.36	0.018	0.55	5.6
	11/03/97	15.45	SUNNY	1.4	0.022	0.69	6.9
Grayrigg Hall Beck	02/05/96	10.00	OVERCAST	2.43	0.031	0.59	6.2
	20/07/96	15.00	SUNNY	Dry	-	-	-
	11/09/96	13.20	OVERCAST	1.06	0.004	0.06	11.9
	12/11/96	13.35	FAIR	3.12	0.049	2.20	6.2
	14/01/97	12.45	SUNNY	1.52	0.014	0.43	5.5
	11/03/97	13.35	SUNNY	1.64	0.018	0.65	6.4

Table A3 (contd.) – Survey details for each site

Site Name	Date	Time	Weather	Width (m)	CSA (m^2)	Q ($m^{-3} sec^{-1}$)	Temp (°C)
Flodder Beck	02/05/96	10.45	OVERCAST	0.72	0.007	0.13	7.4
	20/07/96	15.20	SUNNY	0.21	0.000	0.03	-
	11/09/96	14.05	OVERCAST	0.71	0.004	0.12	12.5
	12/11/96	14.00	OVERCAST	1.33	0.023	1.86	6.1
	14/01/97	13.05	SUNNY	0.62	0.005	0.23	5.9
	11/03/97	14.00	SUNNY	1.12	0.011	0.54	7.1
St Sundays Beck	02/05/96	11.15	OVERCAST	1.32	0.013	0.57	7.5
	20/07/96	15.40	SUNNY	1.23	0.009	0.21	7.4
	11/09/96	14.25	OVERCAST	1.03	0.009	0.22	12.9
	12/11/96	14.15	SHOWERS	1.23	0.020	2.43	5.9
	14/01/97	13.25	SUNNY	1.18	0.011	0.71	5.1
	11/03/97	14.20	SUNNY	1.14	0.011	0.87	7.2
Killington Res Trib	02/05/96	11.50	OVERCAST	1.47	0.015	0.23	7.3
	20/07/96	16.00	SUNNY	1.21	0.009	0.21	8.4
	11/09/96	14.45	OVERCAST	1.42	0.018	0.39	11.7
	12/11/96	14.35	SUNNY	2.53	0.019	0.76	6.4
	14/01/97	13.45	SUNNY	1.76	0.017	0.27	5
	11/03/97	14.45	SUNNY	1.84	0.019	0.32	6.9
River Mint Trib	02/05/96	14.30	SUNNY	1.78	0.022	0.82	7.4
	20/07/96	14.30	SUNNY	1.74	0.012	0.22	8.3
	11/09/96	12.45	OVERCAST	1.62	0.015	0.39	12.2
	12/11/96	12.50	SHOWERS	2.2	0.026	2.34	5.9
	14/01/97	12.05	SUNNY	2.04	0.013	0.70	5.7
	11/03/97	13.00	SUNNY	2.06	0.014	0.73	5.9
Borrow Beck	02/05/96	15.20	SUNNY	2.57	0.069	14.82	9.7
	20/07/96	14.00	SUNNY	1.98	0.022	1.09	10.2
	11/09/96	12.15	OVERCAST	1.26	0.013	0.63	12
	12/11/96	12.15	SUNNY	2.15	0.039	9.25	4.8
	14/01/97	11.40	SUNNY	2.2	0.047	6.90	4.2
	11/03/97	12.15	SUNNY	2.24	0.051	7.78	5.2
Bannisdale Beck	02/05/96	16.30	SUNNY	2.36	0.034	5.60	8.8
	28/07/96	9.40	OVERCAST	1.42	0.015	0.10	5.7
	15/09/96	13.00	SUNNY	1.36	0.018	0.18	13.6
	15/11/96	16.00	FOG	2.51	0.046	2.30	4.6
	17/01/97	15.30	RAIN	2.86	0.043	1.97	4.4
	15/03/97	9.40	OVERCAST	2.42	0.040	1.37	4.8
River Sprint	02/05/96	17.30	SUNNY	4.46	0.051	7.99	7
	17/07/96	11.30	SUNNY	4.21	0.035	4.97	6.7
	15/09/96	12.00	SUNNY	3.32	0.027	2.49	14.2
	14/11/96	16.00	FOG	6.24	0.120	5.70	3.7
	16/01/97	14.45	MISTY	6.29	0.136	2.82	4.7
	15/03/97	10.50	OVERCAST	6.26	0.140	2.89	4.3
Moasdale Beck	03/05/96	9.30	L. CLOUD	4.68	0.100	10.49	4.5
	21/07/96	9.25	L.CLOUD	4.64	0.081	4.31	4.7
	12/09/96	9.40	L. CLOUD	4.62	0.082	4.39	10.6
	13/11/96	9.55	OVERCAST	4.72	0.097	6.81	4.1
	15/01/97	9.25	MISTY	4.39	0.098	5.75	4.2
	12/03/97	9.00	RAIN	4.71	0.110	6.48	3.2
Castle How Beck	03/05/96	10.10	SUNNY	2.56	0.021	1.58	5
	21/07/96	9.50	L. CLOUD	1.94	0.013	0.50	5.6
	12/09/96	9.50	OVERCAST	1.69	0.010	0.29	10.9
	13/11/96	10.25	OVERCAST	2.19	0.020	1.36	4.4
	15/01/97	9.50	MISTY	1.82	0.013	1.01	4.4
	12/03/97	9.30	RAIN	1.8	0.013	1.20	4.6

Table A3 (contd.) – Survey details for each site

Site Name	Date	Time	Weather	Width (m)	CSA (m^2)	Q ($m^{-3} sec^{-1}$)	Temp (°C)
Tarn Beck	03/05/96	11.10	SUNNY	6.72	0.096	4.24	5.2
	21/07/96	10.15	SUNNY	6.22	0.051	3.46	5.7
	12/09/96	10.20	SUNNY	6.32	0.076	2.77	12.1
	13/11/96	10.55	SUNNY	6.44	0.097	5.62	5.4
	15/01/97	10.10	MISTY	6.58	0.064	3.20	4.5
	12/03/97	10.00	MISTY	6.71	0.068	3.35	4.4
Sling Beck	03/05/96	11.45	OVERCAST	1.62	0.019	2.50	5.5
	21/07/96	10.50	SUNNY	1.43	0.011	0.22	5.9
	12/09/96	10.45	SUNNY	1.38	0.009	0.24	11.8
	13/11/96	11.25	SUNNY	2.69	0.040	2.75	5.6
	15/01/97	10.40	MISTY	2.25	0.035	2.76	4.3
	12/03/97	10.35	RAIN	2.32	0.038	2.86	4.9
Holehouse Gill	03/05/96	12.30	SUNNY	2.78	0.051	2.98	7.2
	21/07/96	11.20	SUNNY	2.47	0.020	1.06	6.8
	12/09/96	11.10	SUNNY	2.26	0.027	1.07	10.9
	13/11/96	11.45	SUNNY	2.47	0.033	2.84	5.1
	15/01/97	11.05	MISTY	1.51	0.035	1.36	4.7
	12/03/97	11.00	RAIN	1.64	0.042	1.84	5.1
Crosby Gill	03/05/96	13.10	OVERCAST	4.06	0.056	4.23	8
	21/07/96	11.50	SUNNY	4.31	0.083	1.26	7.8
	12/09/96	11.40	SUNNY	4.18	0.068	1.07	12.6
	13/11/96	12.15	OVERCAST	5.03	0.124	6.05	4.8
	15/01/97	11.30	MISTY	4.76	0.104	2.75	4.6
	12/03/97	11.35	MISTY	4.89	0.113	3.06	5.6
Greendale Gill	03/05/96	14.00	RAIN	4.34	-	4.62 *	5.7
	21/07/96	12.35	SUNNY	4.4	0.057	3.36	9.4
	12/09/96	12.55	OVERCAST	4.26	0.027	2.16	12.8
	13/11/96	12.55	OVERCAST	6.14	0.058	4.64	5.4
	15/01/97	12.15	MISTY	5.07	0.059	2.40	4.1
	12/03/97	12.20	MISTY	5.21	0.068	2.66	4.8
Nether Beck	03/05/96	14.45	OVERCAST	8.17	-	12.69 *	6.4
	21/07/96	13.00	SUNNY	7.84	0.096	5.19	8.5
	12/09/96	13.15	OVERCAST	6.82	0.119	4.76	11.3
	13/11/96	13.25	OVERCAST	7.36	0.128	12.33	5.3
	15/01/97	13.00	MISTY	6.35	0.130	9.39	4.2
	12/03/97	12.55	MISTY	6.38	0.068	2.66	4.9
Whillan Beck	03/05/96	15.30	OVERCAST	1.22	-	8.29 *	7.2
	21/07/96	14.05	SUNNY	1.25	0.077	4.22	8.6
	12/09/96	14.00	BRIGHT	1.21	0.045	2.46	11.7
	13/11/96	14.00	OVERCAST	1.24	0.077	10.63	4.3
	15/01/97	13.45	SUNNY	1.49	0.061	4.68	4.5
	12/03/97	13.40	MISTY	1.51	0.064	5.28	7
Hardknott Gill	03/05/96	16.15	OVERCAST	2.43	-	1.84 *	7.7
	21/07/96	14.45	SUNNY	2.13	0.022	1.17	8.4
	12/09/96	14.20	SUNNY	1.94	0.025	0.97	11.4
	13/11/96	14.35	OVERCAST	2.98	0.033	2.02	4.8
	15/01/97	14.10	SUNNY	2.87	0.034	0.86	4.9
	12/03/97	14.15	MISTY	2.94	0.037	1.02	5.3
Whelpside Gill	04/05/96	8.50	SUNNY	2.36	-	1.44 *	3.6
	21/07/96	16.00	L. CLOUD	2.12	0.016	0.50	8.5
	13/09/96	9.20	OVERCAST	2.06	0.011	0.29	8.4
	14/11/96	9.10	MISTY	2.79	0.025	1.97	3.5
	16/01/97	9.10	OVERCAST	2.17	0.016	0.82	4.1
	13/03/97	8.50	OVERCAST	2.27	0.020	1.15	3.4

Table A3 (contd.) – Survey details for each site

Site Name	Date	Time	Weather	Width (m)	CSA (m^2)	Q ($m^{-3} sec^{-1}$)	Temp (°C)
Wyth Burn	04/05/96	9.30	SUNNY	4.92	-	4.85 *	6.1
	21/07/96	16.25	OVERCAST	2.48	0.020	0.40	7.9
	13/09/96	9.45	SUNNY	2.64	0.030	0.43	8.5
	14/11/96	9.30	OVERCAST	4.96	0.082	8.11	4.6
	16/01/97	9.25	OVERCAST	2.63	0.043	3.29	3.9
	13/03/97	9.25	OVERCAST	2.81	0.048	3.74	3.7
Launchy Ghyll	04/05/96	10.00	SUNNY	1.92	-	2.76 *	3.8
	21/07/96	16.50	OVERCAST	1.89	0.066	0.49	5.7
	13/09/96	10.05	SUNNY	1.82	0.067	0.64	8
	14/11/96	9.55	OVERCAST	2.46	0.104	5.50	5
	16/01/97	9.55	OVERCAST	1.78	0.059	1.21	3.8
	13/03/97	9.50	OVERCAST	1.84	0.058	1.26	4.2
Shoulthwaite Gill	04/05/96	10.35	SUNNY	2.97	-	2.09 *	5.4
	21/07/96	17.20	SUNNY	2.04	0.026	0.40	7.9
	13/09/96	10.40	SUNNY	1.93	0.031	0.39	8.3
	14/11/96	10.20	OVERCAST	2.15	0.050	3.86	5.2
	16/01/97	10.30	OVERCAST	1.92	0.037	1.01	4.3
	13/03/97	10.20	RAIN	1.98	0.042	1.22	5.3
Coledale Beck	04/05/96	11.25	SUNNY	5.49	-	5.14 *	8.2
	27/07/96	14.35	OVERCAST	3.82	0.062	2.10	4.9
	13/09/96	11.20	SUNNY	4.56	0.069	1.32	8.7
	14/11/96	11.25	OVERCAST	5.62	0.159	9.42	4.8
	16/01/97	11.00	OVERCAST	3.82	0.079	0.08	4.7
	13/03/97	10.55	OVERCAST	3.94	0.086	2.20	5.8
Liza Beck	04/05/96	14.00	OVERCAST	2.94	-	10.09 *	7.2
	27/07/96	15.20	OVERCAST	3.06	0.030	3.36	4.2
	13/09/96	12.00	SUNNY	2.84	0.037	4.24	9
	14/11/96	11.55	MISTY	3.84	0.076	13.34	3.6
	16/01/97	11.30	OVERCAST	2.7	0.045	5.13	4.8
	13/03/97	11.40	OVERCAST	2.76	0.051	7.14	3.7
Mill Beck 2	04/05/96	14.55	OVERCAST	3.06	-	3.89 *	8.3
	27/07/96	15.50	OVERCAST	2.72	0.041	1.20	5.6
	13/09/96	12.30	SUNNY	2.38	0.023	1.06	10.2
	14/11/96	12.25	MISTY	3.86	0.068	6.65	5.6
	16/01/97	11.55	OVERCAST	2.5	0.038	1.83	4.2
	13/03/97	12.00	OVERCAST	2.57	0.042	2.05	5.3
Sour Milk Gill	04/05/96	15.45	OVERCAST	3.82	-	2.82 *	5.9
	27/07/96	16.35	OVERCAST	2.87	0.025	1.05	4.7
	13/09/96	13.55	SUNNY	2.84	0.025	0.57	11.5
	14/11/96	13.30	OVERCAST	3.75	0.045	3.41	3.8
	16/01/97	12.25	OVERCAST	3.85	0.034	2.03	4.3
	13/03/97	12.45	RAIN	3.89	0.036	2.23	4.9
Styhead Gill	04/05/96	16.25	OVERCAST	6.62	-	7.33 *	6.4
	27/07/96	17.00	OVERCAST	5.97	0.066	2.14	5.7
	13/09/96	14.05	SUNNY	5.95	0.063	1.39	13.1
	14/11/96	13.50	OVERCAST	10.28	0.162	8.22	4.1
	16/01/97	12.45	OVERCAST	10.22	0.119	6.21	4.6
	13/03/97	13.15	RAIN	10.27	0.123	6.17	5
Glenridding Beck	05/05/96	9.25	SUNNY	2.92	-	6.81 *	4.7
	20/07/96	9.45	SUNNY	1.2	0.013	1.34	6.2
	14/09/96	9.30	SUNNY	1.26	0.035	2.96	9.2
	15/11/96	9.15	OVERCAST	1.44	0.055	10.29	4.1
	17/01/97	9.30	RAIN	1.64	0.040	3.61	4.7
	14/03/97	9.05	OVERCAST	1.75	0.047	4.23	3.1

Table A3 (contd.) – Survey details for each site

Site Name	Date	Time	Weather	Width (m)	CSA (m^2)	Q ($m^{-3}sec^{-1}$)	Temp (^oC)
Glencoyne Beck	05/05/96	10.05	SUNNY	3.86	-	4.27 *	5.3
	20/07/96	10.10	SUNNY	3.82	0.049	1.87	7.1
	14/09/96	10.00	SUNNY	3.85	0.050	1.71	9.7
	15/11/96	10.05	MISTY	4.02	0.070	5.63	5.1
	17/01/97	9.50	RAIN	2.88	0.037	2.28	4.9
	14/03/97	9.40	OVERCAST	2.94	0.040	2.56	4.2
Aira Beck	05/05/96	10.45	BRIGHT	5.02	-	7.36 *	5.7
	27/07/96	12.35	OVERCAST	4.98	0.048	0.90	4.9
	14/09/96	10.30	SUNNY	5.06	0.053	1.03	9.8
	15/11/96	10.35	MISTY	4.07	0.073	7.71	4.5
	17/01/97	10.20	RAIN	4.54	0.092	7.30	4.6
	14/03/97	10.15	RAIN	4.55	0.093	7.28	4.5
Parkhouse Gill	05/05/96	11.20	SUNNY	2.58	-	1.44 *	6.6
	20/07/96	10.55	SUNNY	2.02	0.012	0.35	6.4
	14/09/96	10.55	SUNNY	1.94	0.013	0.37	9.3
	15/11/96	11.00	OVERCAST	1.96	0.029	2.18	5.5
	17/01/97	10.45	RAIN	2.38	0.021	0.88	4.8
	14/03/97	10.40	OVERCAST	2.51	0.022	0.96	4.9
Fusedale Beck	05/05/96	12.00	SUNNY	1.85	-	4.39 *	7.6
	27/07/96	11.35	OVERCAST	1.67	0.018	0.60	5.2
	14/09/96	11.30	SUNNY	1.56	0.019	0.64	12.3
	15/11/96	11.35	OVERCAST	1.71	0.032	6.79	4.8
	17/01/97	11.20	RAIN	2.17	0.021	2.97	4.9
	14/03/97	11.10	OVERCAST	2.24	0.024	3.46	5.3
Heltondale Beck	05/05/96	13.00	SUNNY	2.46	-	4.12 *	8.6
	20/07/96	11.40	SUNNY	1.84	0.017	0.71	9.2
	14/09/96	12.20	SUNNY	1.95	0.024	0.76	12.6
	15/11/96	12.00	OVERCAST	2.93	0.058	9.67	5.1
	17/01/97	12.10	RAIN	2.24	0.031	1.20	4.7
	14/03/97	12.00	SUNNY	2.32	0.034	1.22	6.2
Cawdale Beck	05/05/96	13.45	SUNNY	2.06	-	3.75 *	9.6
	20/07/96	12.15	SUNNY	1.88	0.051	1.77	9.8
	14/09/96	13.05	SUNNY	1.86	0.043	1.59	14.6
	15/11/96	12.30	OVERCAST	2.26	0.047	5.91	5.4
	17/01/97	12.45	RAIN	1.94	0.036	1.33	4.8
	14/03/97	12.35	OVERCAST	1.92	0.017	0.40	6.4
Gatescarth Beck	05/05/96	14.30	SUNNY	3.72	-	1.74 *	9.2
	27/07/96	10.35	OVERCAST	3.91	0.017	0.40	5.1
	14/09/96	13.30	SUNNY	3.49	0.024	0.42	12.7
	15/11/96	13.30	OVERCAST	2.32	0.048	1.80	4.5
	17/01/97	13.20	RAIN	2.65	0.044	1.44	4.8
	14/03/97	13.10	OVERCAST	2.74	0.048	1.66	5.6
Naddle Beck	05/05/96	15.15	SUNNY	3.56	-	3.34 *	9.4
	20/07/96	12.45	SUNNY	2.86	0.033	0.57	10.6
	14/09/96	14.00	SUNNY	2.84	0.016	0.31	10.3
	15/11/96	13.30	OVERCAST	2.32	0.032	4.34	4.5
	17/01/97	13.50	RAIN	2.96	0.027	2.95	4.5
	14/03/97	13.40	OVERCAST	3	0.029	2.81	5.3
Mosedale Beck	05/05/96	15.55	SUNNY	6.48	-	4.88 *	9.6
	27/07/96	9.55	OVERCAST	4.16	0.038	1.06	4.7
	14/09/96	14.30	OVERCAST	3.8	0.026	0.84	15.8
	15/11/96	14.25	OVERCAST	4.89	0.087	4.36	3.9
	17/01/97	14.05	RAIN	5.46	0.125	4.93	4.7
	14/03/97	14.10	OVERCAST	6.02	0.141	4.88	5.4

Table A3 (contd.) – Survey details for each site

Site Name	Date	Time	Weather	Width (m)	CSA (m^2)	Q ($m^{-3} sec^{-1}$)	Temp (°C)
Tailbert Gill	05/05/96	16.30	OVERCAST	1.46	-	0.44 *	10.6
	20/07/96	13.15	SUNNY	1.42	0.017	0.13	10.4
	14/09/96	15.05	BRIGHT	1.32	0.006	0.10	15.1
	15/11/96	15.15	OVERCAST	1.64	0.019	0.51	6.1
	17/01/97	14.25	RAIN	1.44	0.016	0.34	5.4
	14/03/97	14.40	OVERCAST	1.49	0.018	0.35	5.8

NOTE:

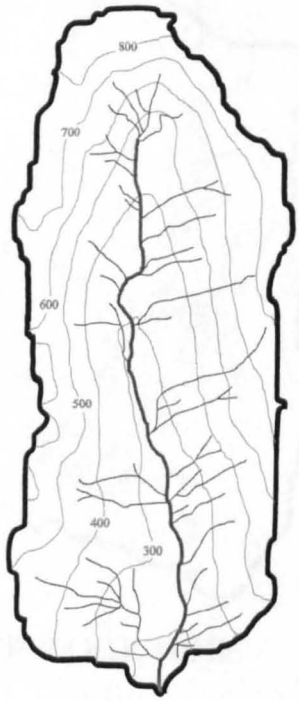
Sites with an asterisk next to the discharge value experienced a malfunction of the flowmeter on the first trip. Therefore, the first month's discharge is based on an extrapolation of the amount of discharge in May at the other completed sites. May flow constituted 23.3% of the total survey discharge thus by dividing the flow from the complete five months by 0.767 gives you a complete annual discharge. It is then possible to calculate an extrapolated 'May' discharge for the sites with missing values by finding how much of the 'recalculated' annual discharge that 23.3% represents.

A.3 Catchment Characteristic maps

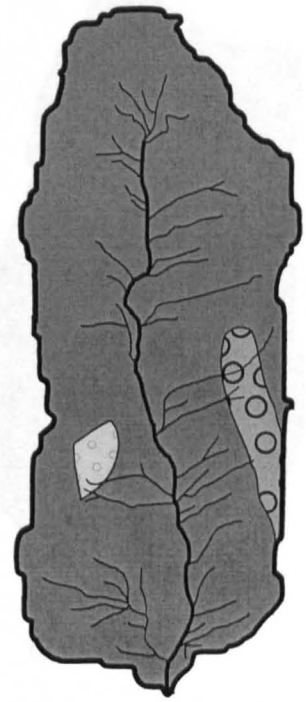
For the purpose of the study, each catchment was digitised and the catchment characteristics were derived using the Geographical Information System package, Arc/Info (see Chapter 4). Maps of the individual catchments showing topography, geology and soils can be found in Figures A3 to A57 (Land use can be found in Table F2).

N.B. The top of the page is North and the scale varies.

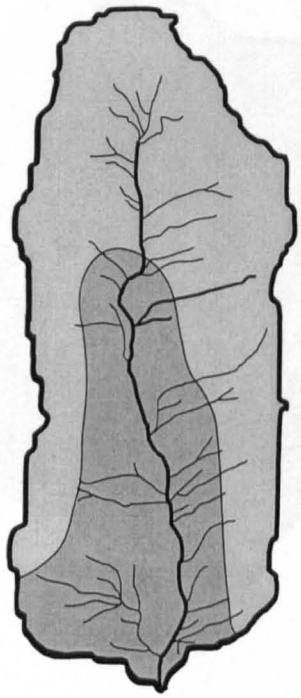
Figure A.3 - Catchment characteristics of Rydal Beck (Site 1)



TOPOGRAPHY



GEOLOGY



SOILS

KEY:

Rhyolite (BVG)

Tuffs (BVG)

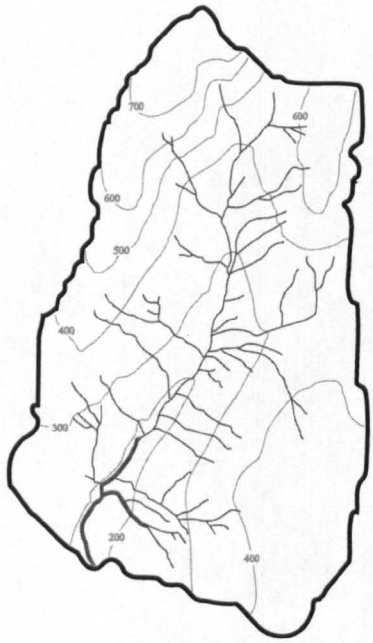
Andesite (BVG)

Humic Ranker

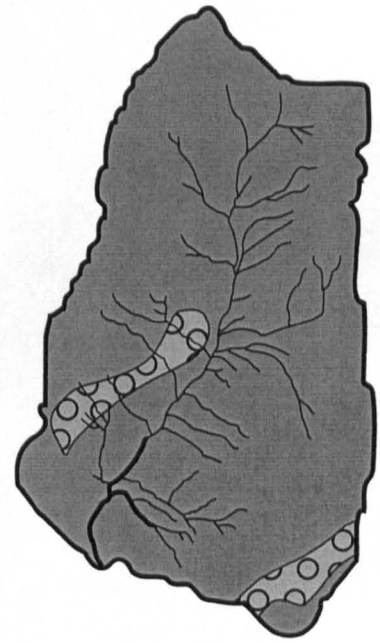
Typical Brown Podzol

1000m

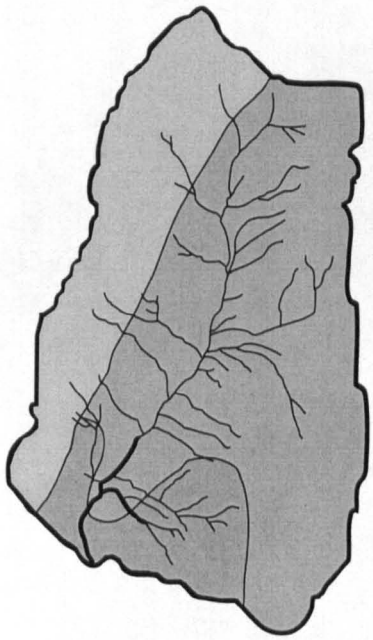
Figure A.4 - Catchment characteristics of Stock Ghyll (Site 2)



TOPOGRAPHY



GEOLOGY



SOILS

KEY:

Andesite (BVG)

Tuffs (BVG)

Humic Ranker

Stagnohumic Gley

Typical Brown Podzol

1000m

Figure A.5 - Catchment characteristics of How Beck (Site 3)

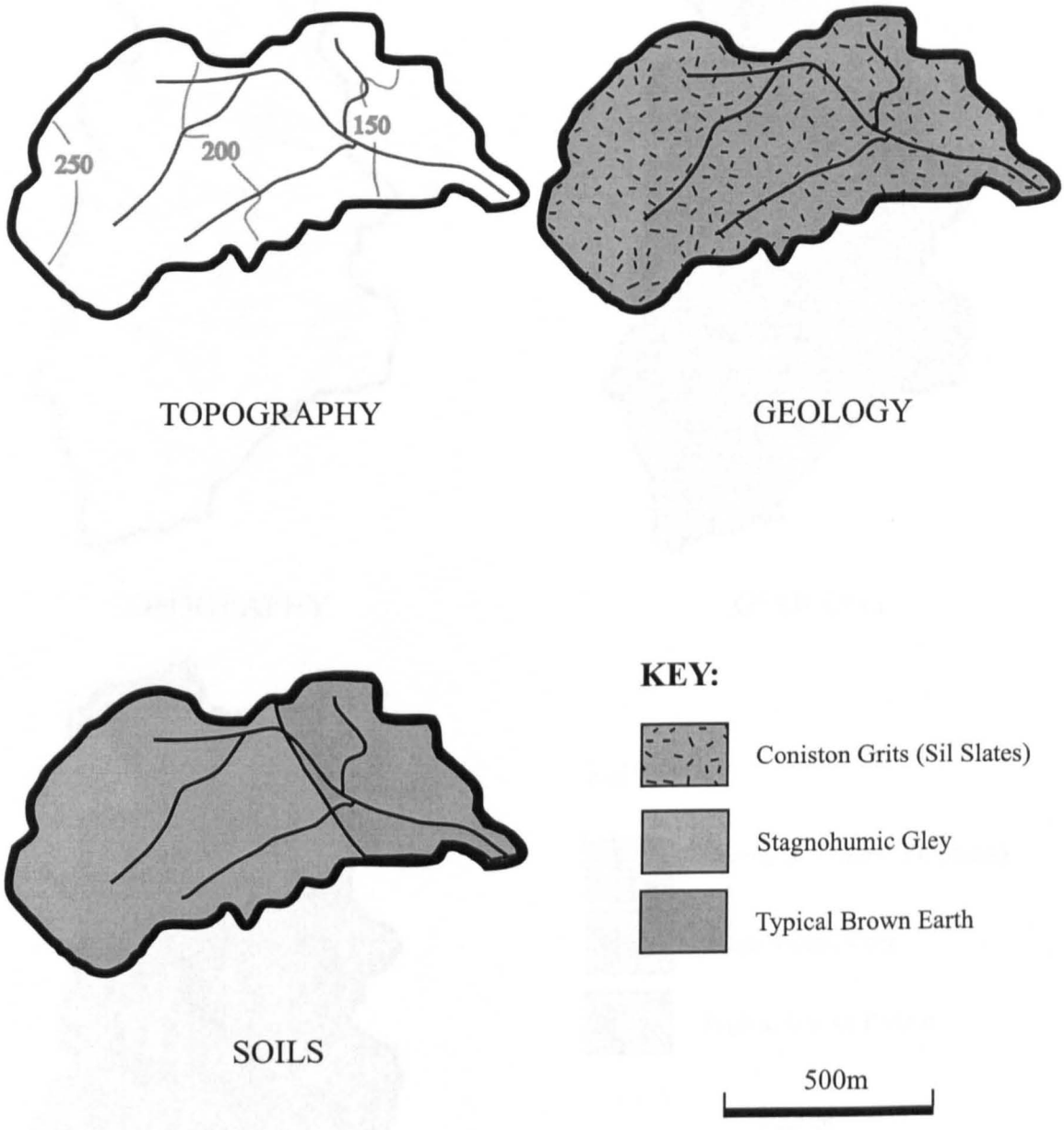
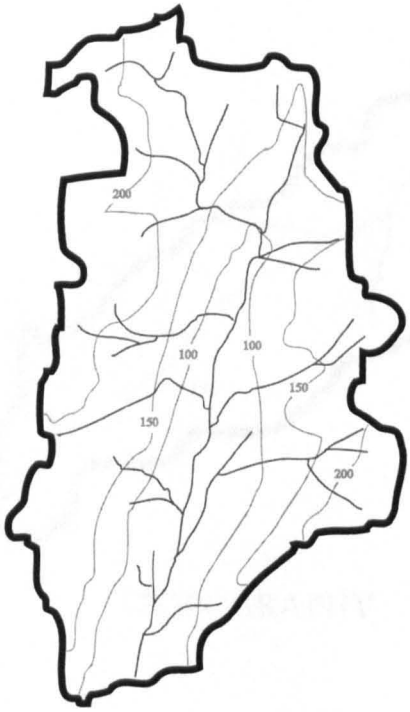


Figure A.6 - Catchment characteristics of Dale Park Beck (Site 4)



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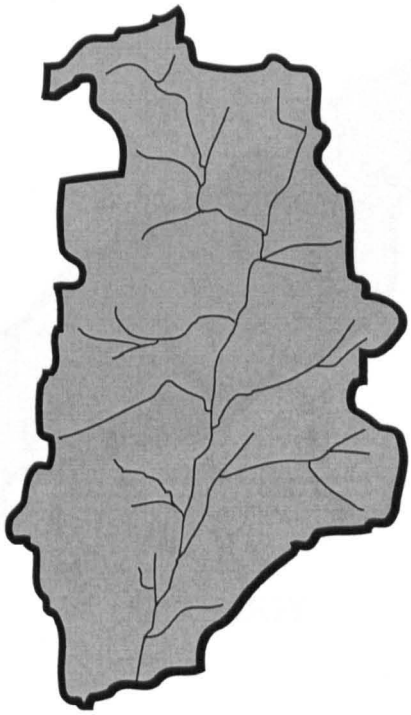
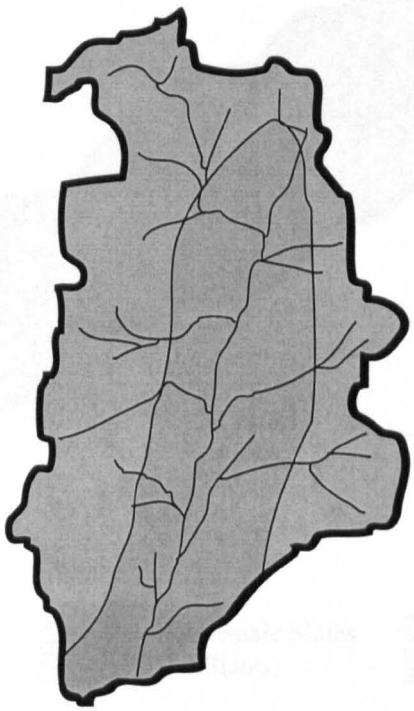


GEOLOGY



SOILS

KEY:

Bannisdale Slates (Sil Slates)

Stagnohumic Gley

Typical Brown Podzol

1000m

Figure A.7 - Catchment characteristics of Low Cunsey Beck (Site 5)

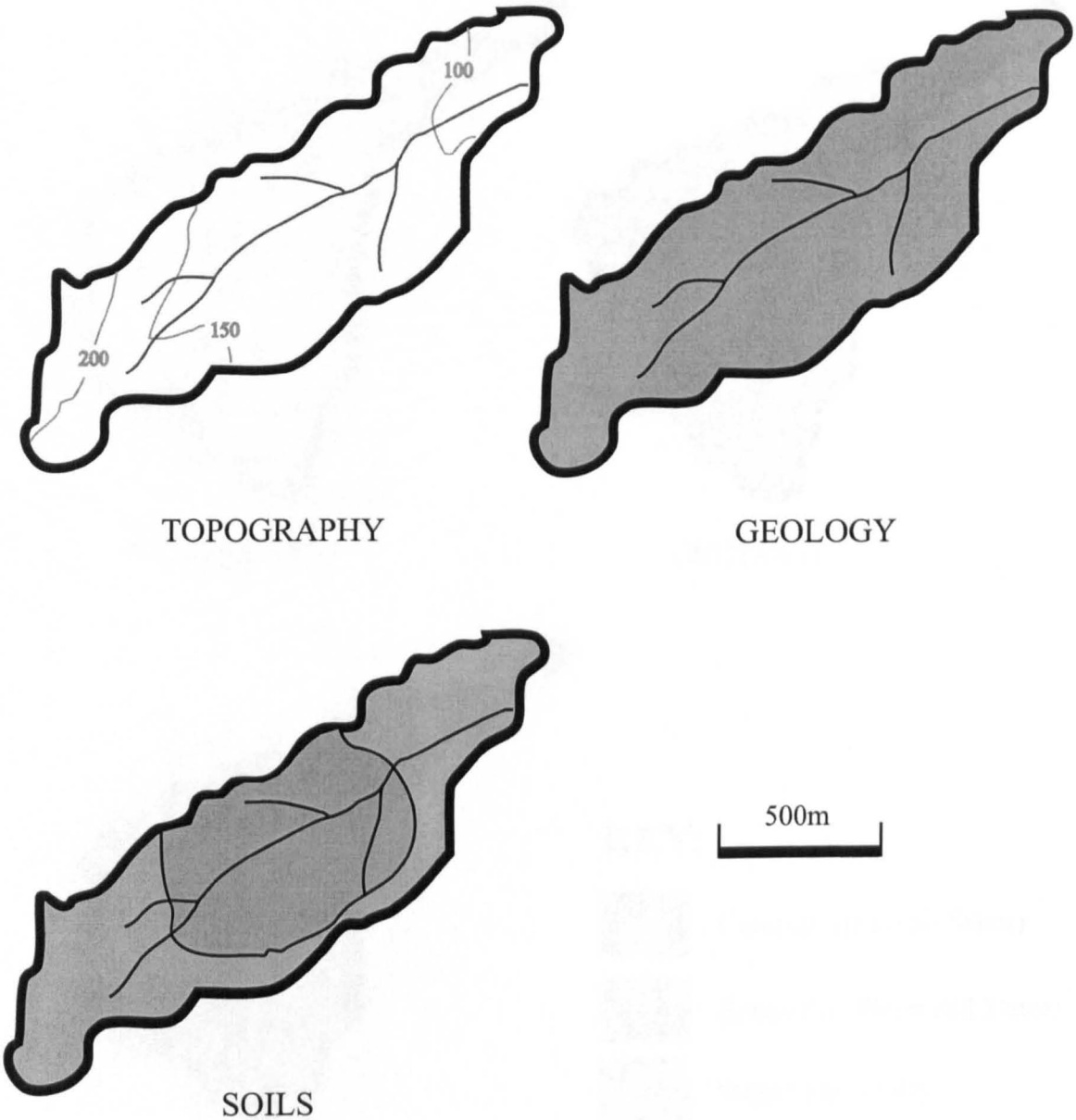
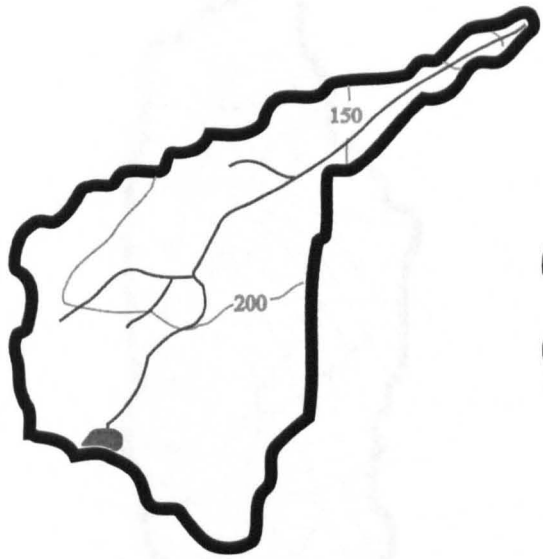


Figure A.8 - Catchment characteristics of Belle Grange Beck (Site 6)



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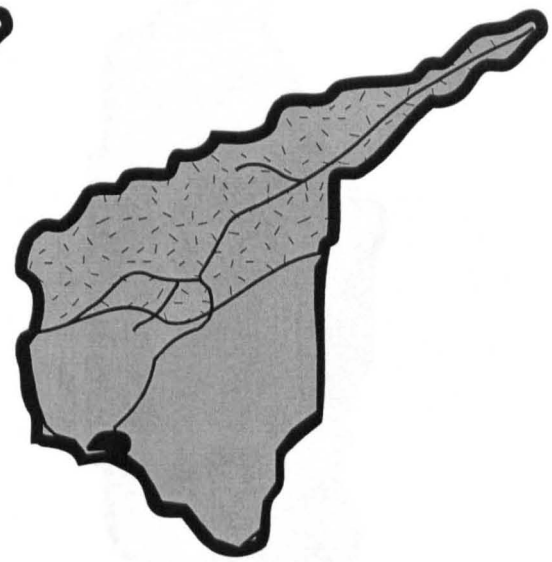
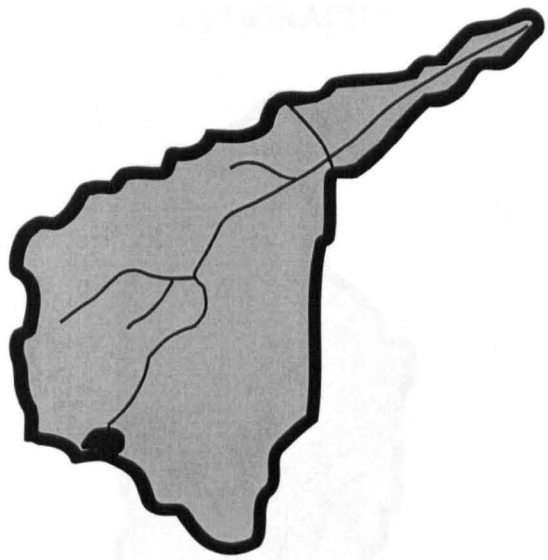


GEOLOGY



SOILS

KEY:

Coniston Grits (Sil Slates)

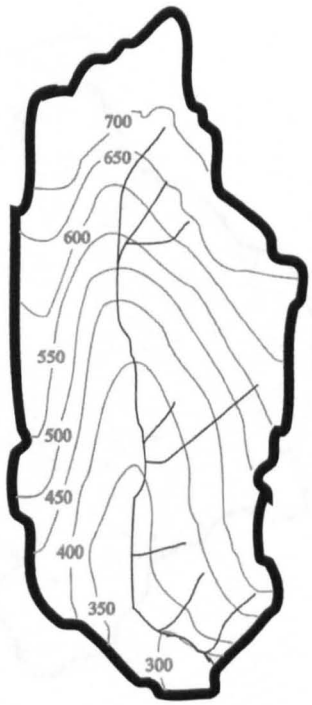
Bannisdale Slates (Sil Slates)

Stagnohumic Gley

Typical Brown Podzol

500m

Figure A.9 - Catchment characteristics of Red Dell Beck (Site 7)



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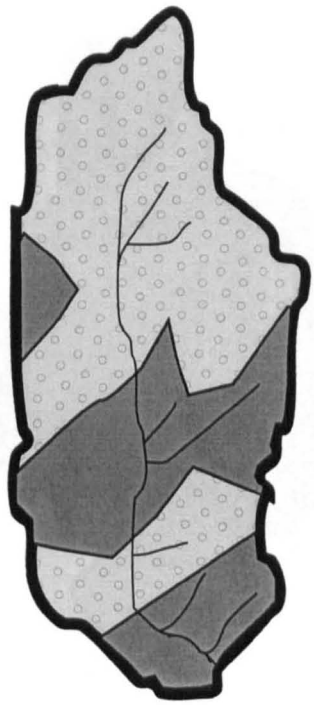
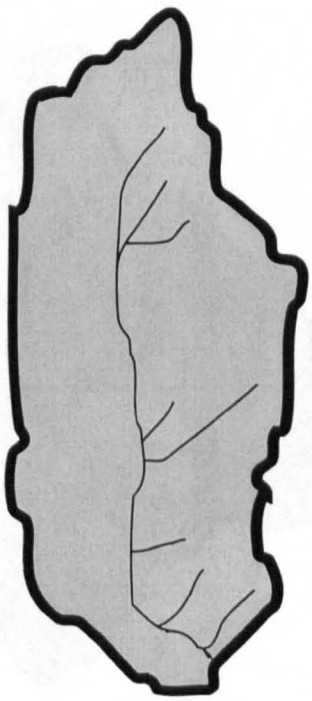


GEOLOGY



SOILS

KEY:

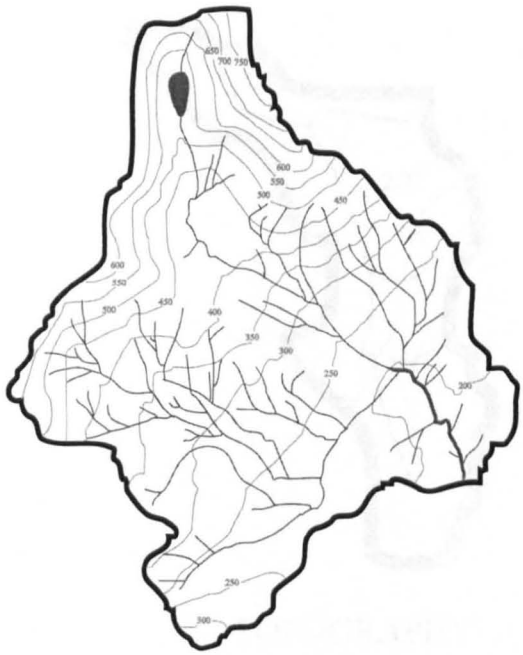
Rhyolite (BVG)

Tuffs (BVG)

Humic Ranker

500m

Figure A.10 - Catchment characteristics of Torver Beck (Site 8)



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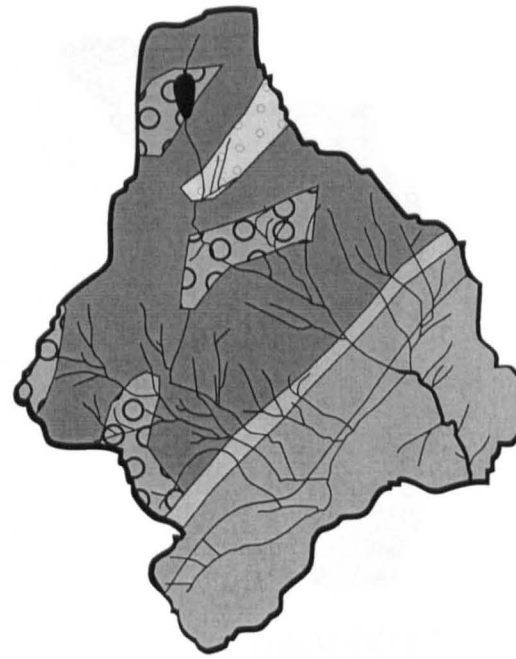

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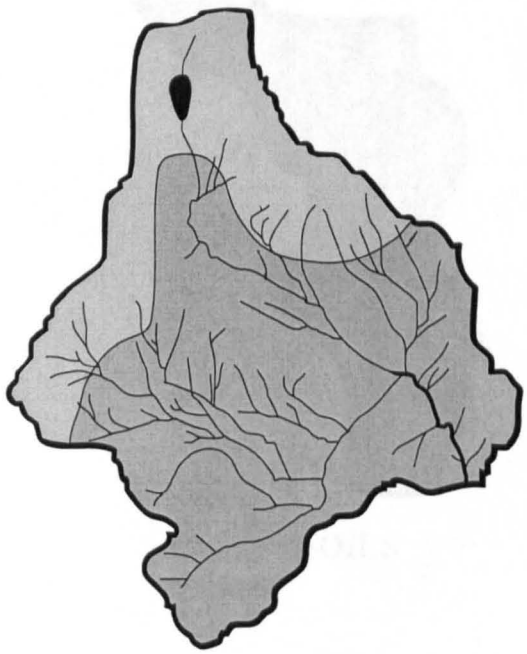


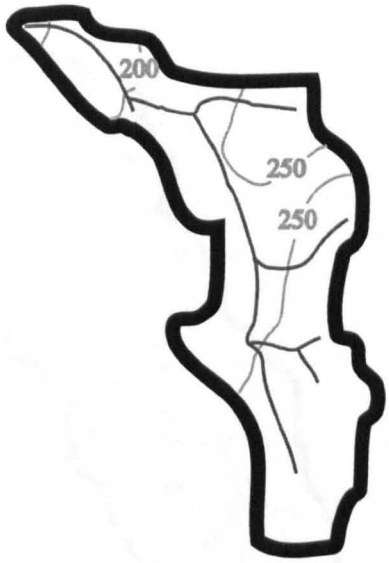
SOILS

KEY:

- Rhyolite (BVG)
- Tuffs (BVG)
- Andesite (BVG)
- Coniston Limestone (Sil Slates)
- Stockdale Shales (Sil Slates)
- Brathay Flags (Sil Slates
- Stagnohumic Gley
- Humic Ranker

1000m

Figure A.11 - Catchment characteristics of Washfall Beck (Site 9)



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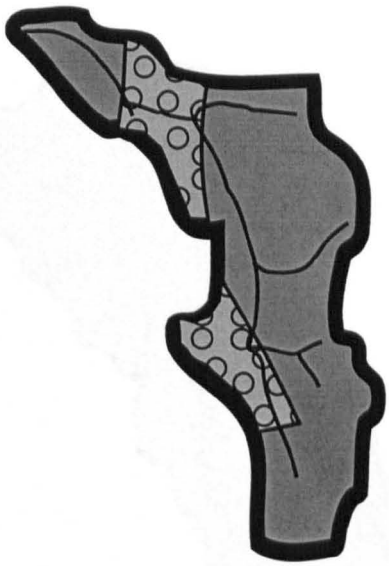

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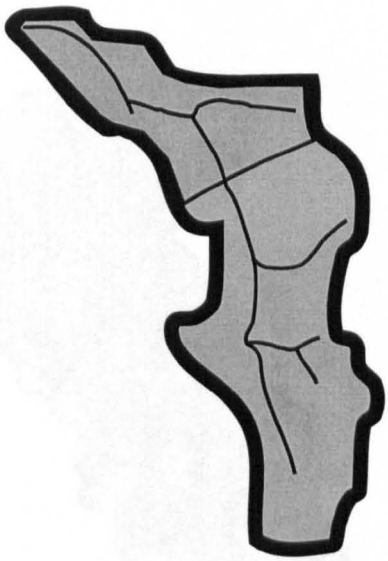


SOILS

KEY:

Andesite (BVG)

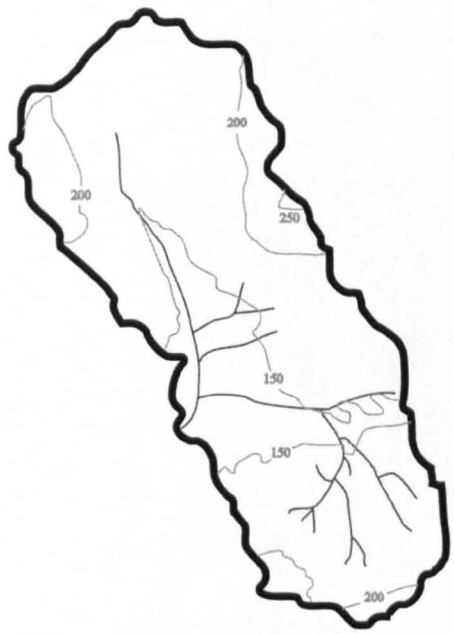
Tuffs (BVG)

Typical Brown Podzol

Stagnohumic Gley

500m

Figure A.12 - Catchment characteristics of Mill Beck 1 (Site 10)



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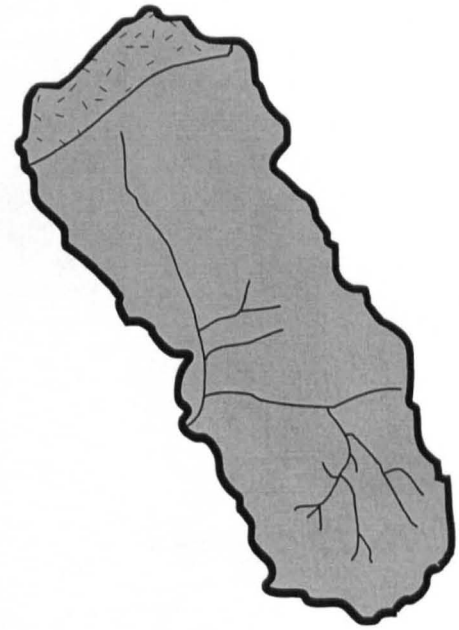
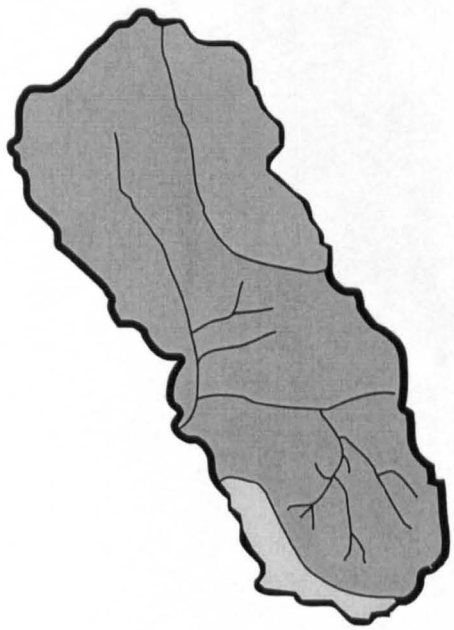


GEOLOGY



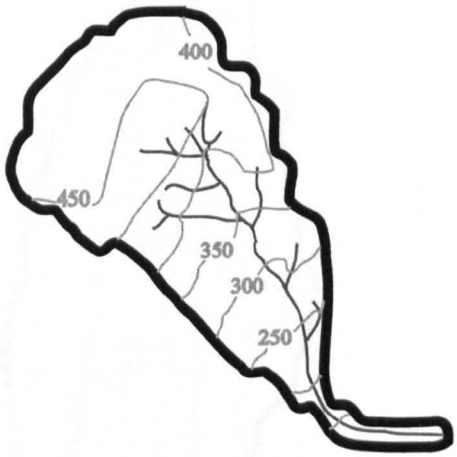
SOILS

KEY:

- Bannisdale Slates (Sil Slates)
- Coniston Grits (Sil Slates)
- Typical Brown Earth
- Typical Brown Podzol
- Brown Ranker

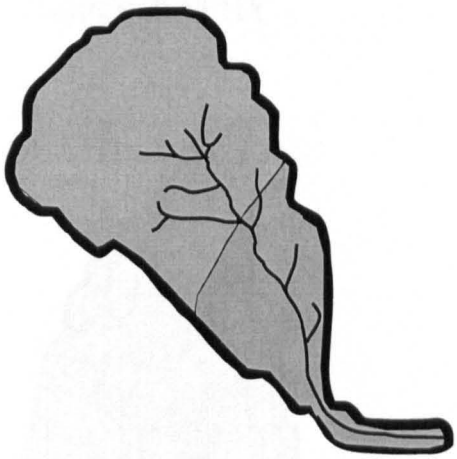
1000m

Figure A.13 - Catchment characteristics of Stony Beck (Site 11)



TOPOGRAPHY

GEOLOGY



SOILS

KEY:

Rhyolite (BVG)

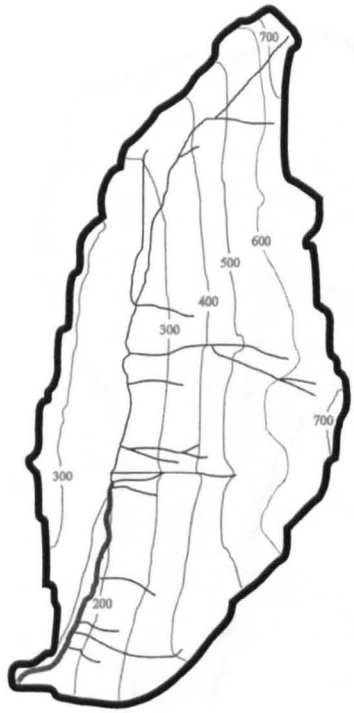
Tuffs (BVG)

Stagnohumic Gley

Typical Brown Podzol

500m

Figure A.14 - Catchment characteristics of Hagg Beck (Site 12)



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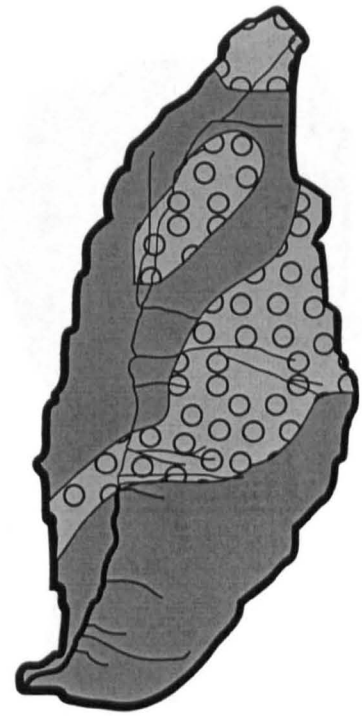

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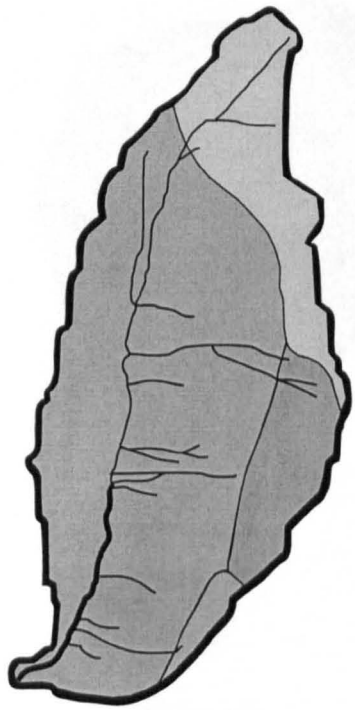


SOILS

KEY:

- Rhyolite (BVG)
- Tuffs (BVG)
- Typical Brown Podzol
- Humic Ranker
- Raw Oligofibrous Peat
- Stagnohumic Gley

1000m

Figure A.15 - Catchment characteristics of Trout Beck (Site 13)

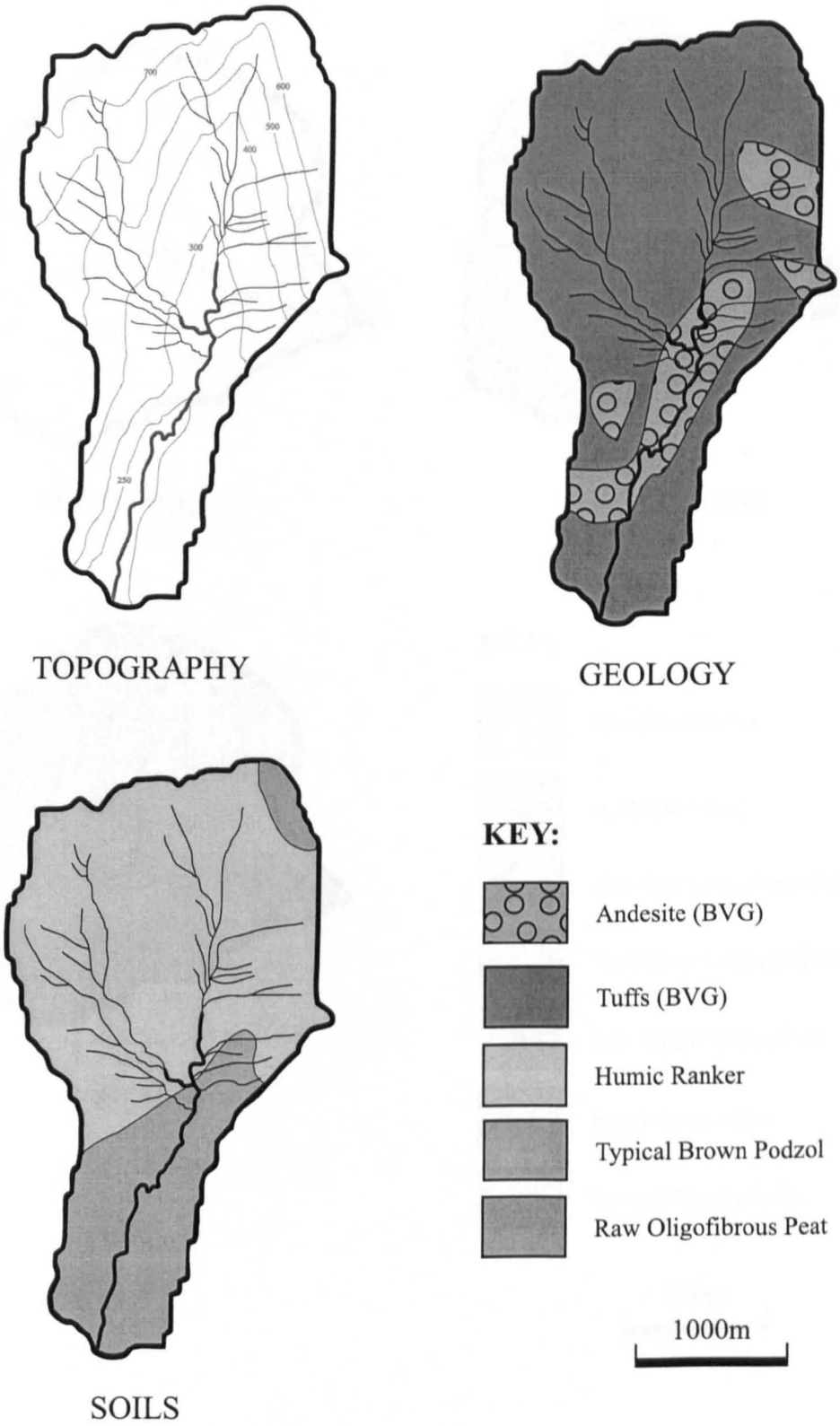
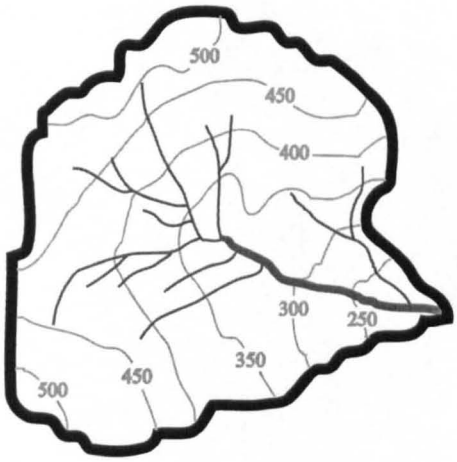


Figure A.17 - Catchment characteristics of Hall Gill (Site 15)



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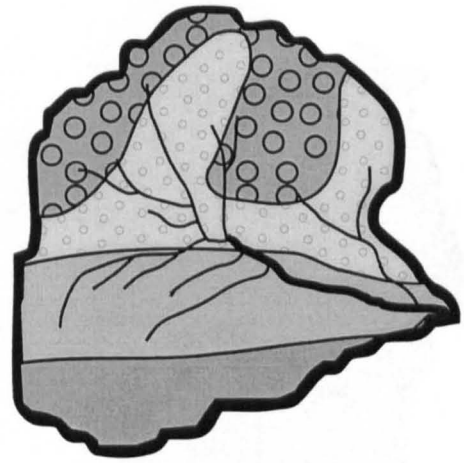
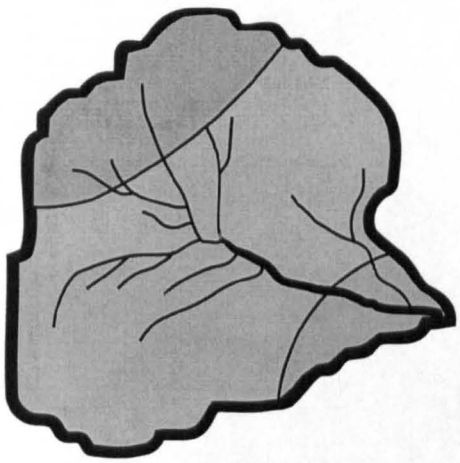


GEOLOGY



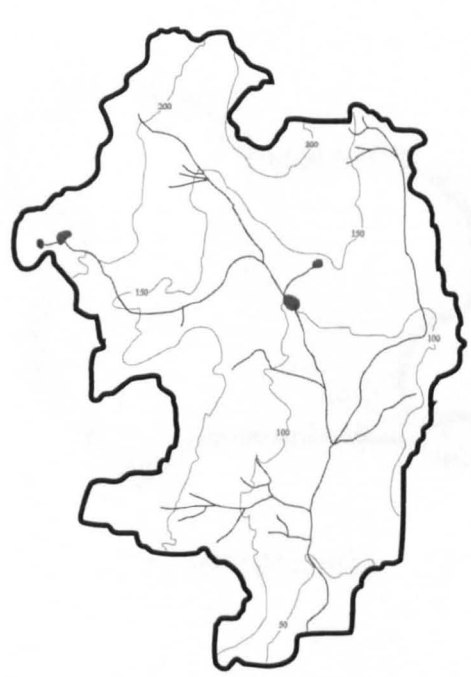
SOILS

KEY:

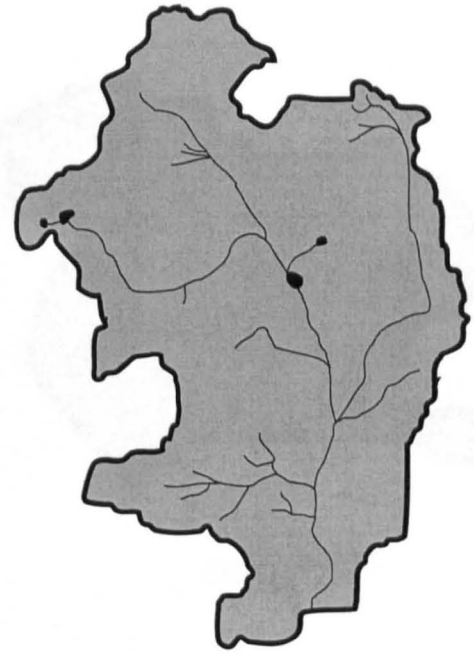
- Rhyolite (BVG)
- Andesite (BVG)
- Coniston Limestone (Sil Slates)
- Stockdale Shales (Sil Slates)
- Raw Oligofibrous Peat
- Stagnohumic Gley
- Typical Brown Podzol

500m

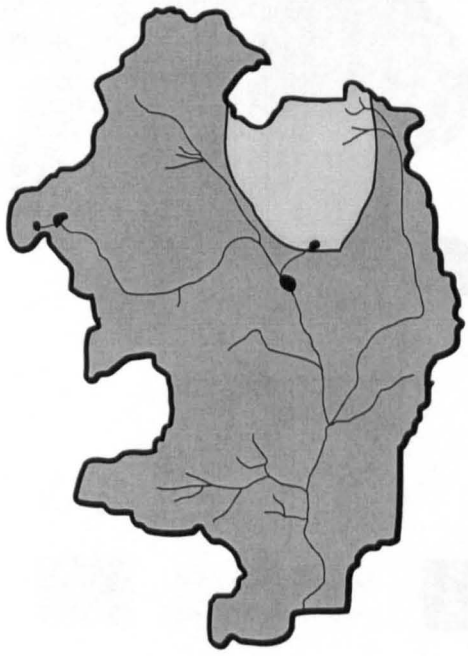
Figure A.18 - Catchment characteristics of Chapel Beck (Site 16)



TOPOGRAPHY



GEOLOGY



SOILS

KEY:

Bannisdale Slates (Sil Slates)

Typical Brown Earth

Brown Ranker

1000m

Figure A.19 - Catchment characteristics of Chapel Beck Tributary (Site 17)

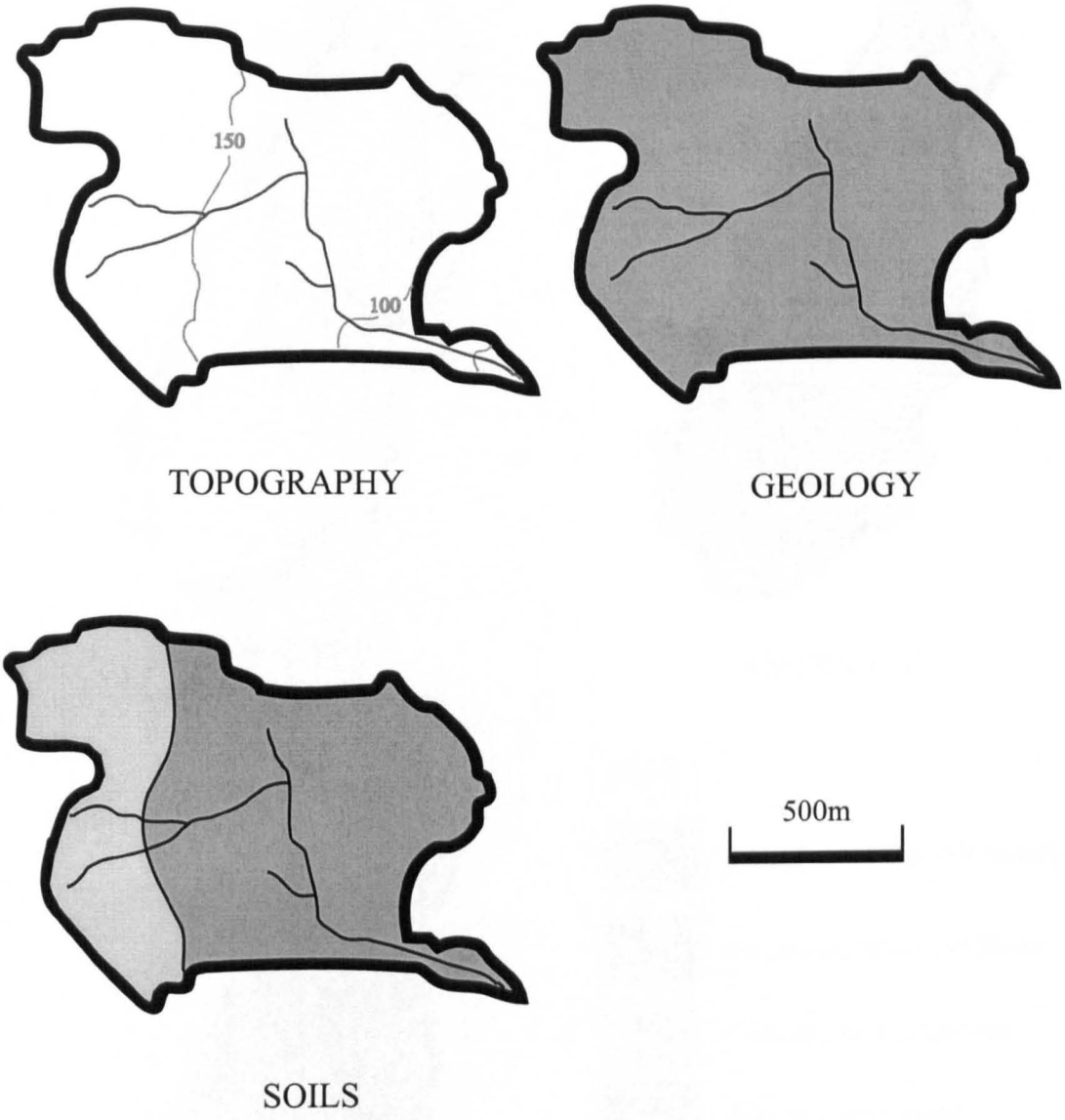
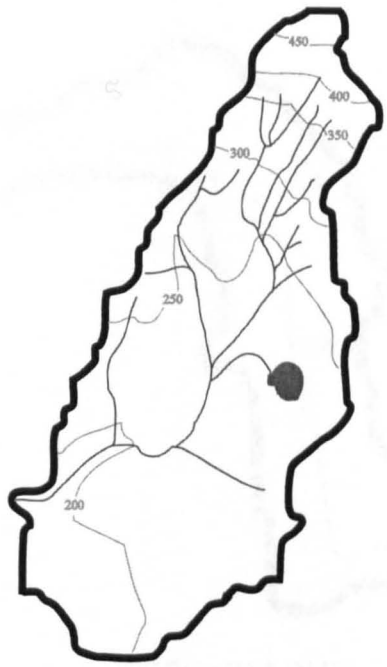


Figure A.20 - Catchment characteristics of Grayrigg Hall Beck (Site 18)



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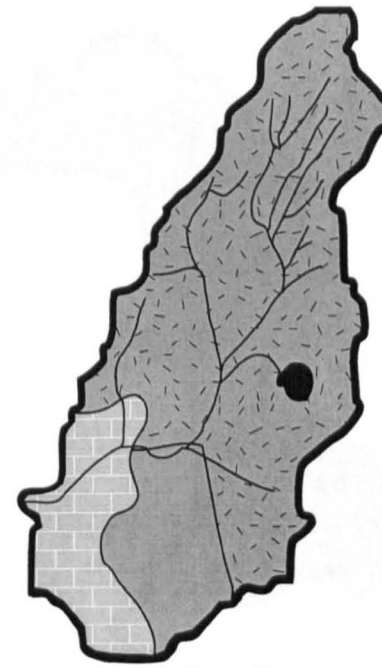
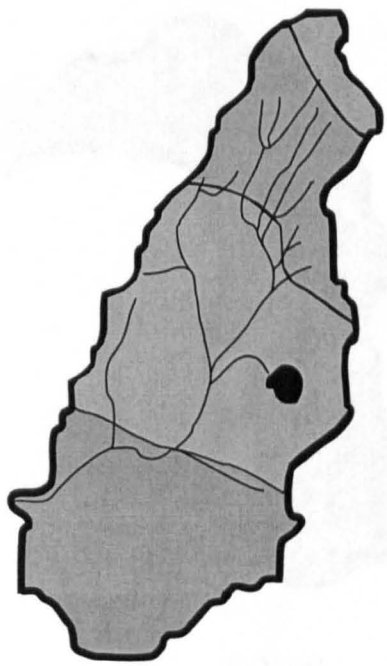


GEOLOGY



SOILS

KEY:

- Kirby Moor Flags (Sil Slates)
- Bannisdale Slates (Sil Slates)
- Carboniferous Limestone
- Typical Brown Earth
- Cambic Stagnogley
- Typical Brown Podzol
- Ferric Stagnopodzol

1000m

Figure A.21 - Catchment characteristics of Flodder Beck (Site 19)

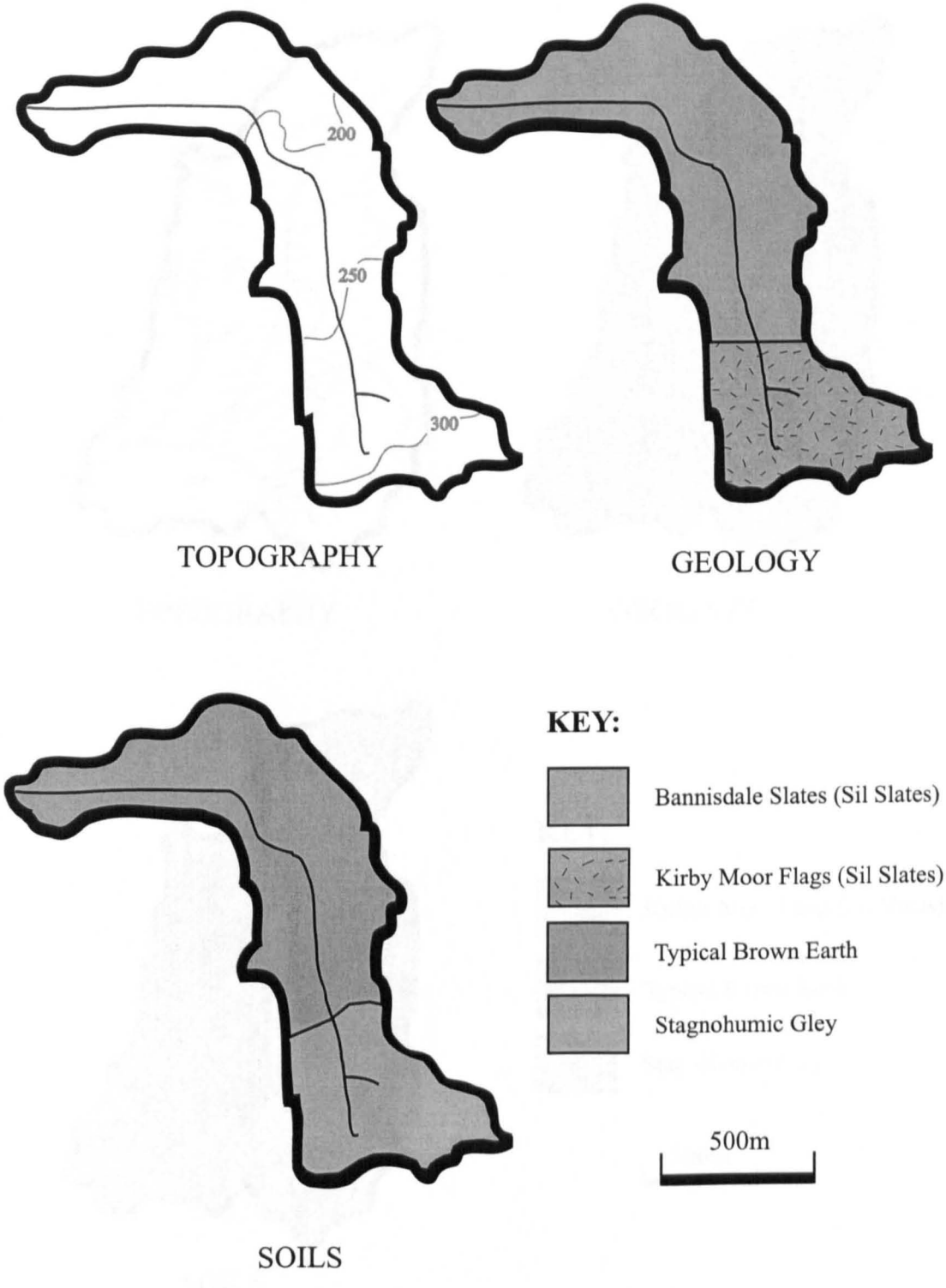


Figure A.22 - Catchment characteristics of St Sundays Beck (Site 20)

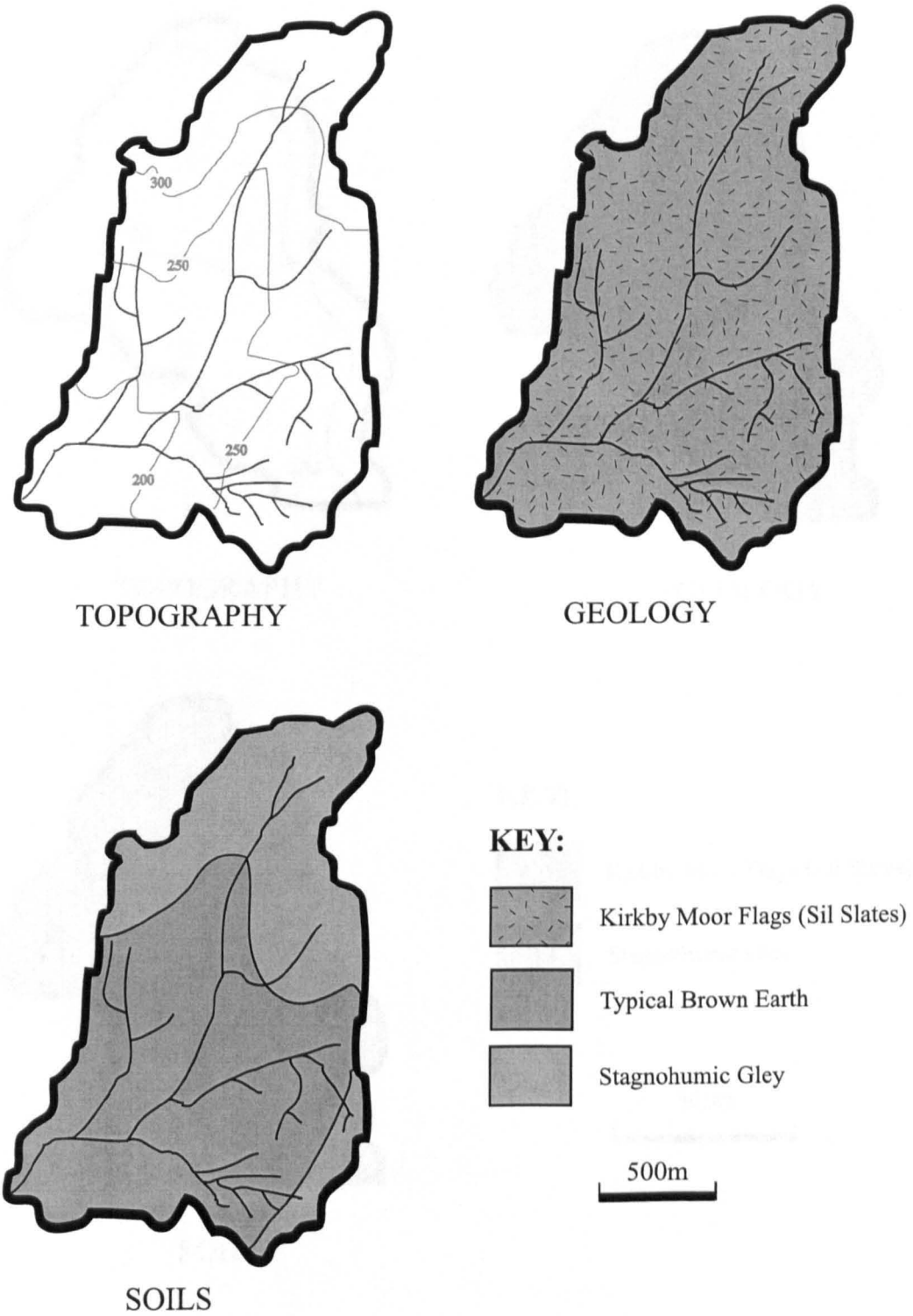
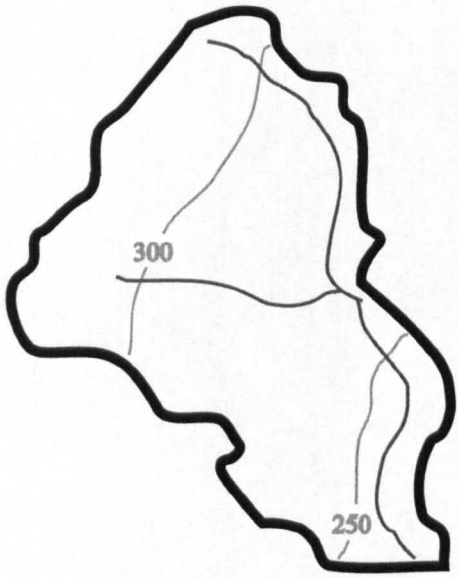
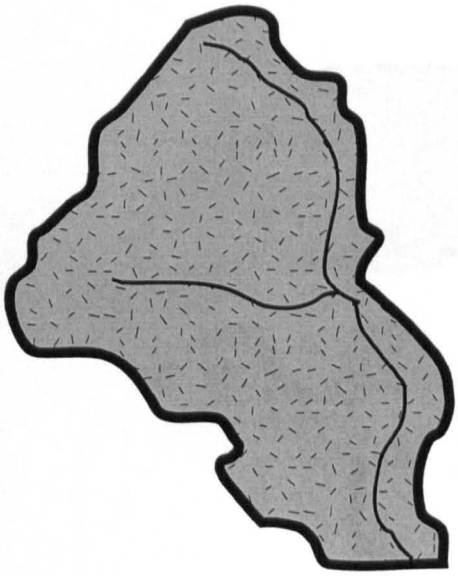


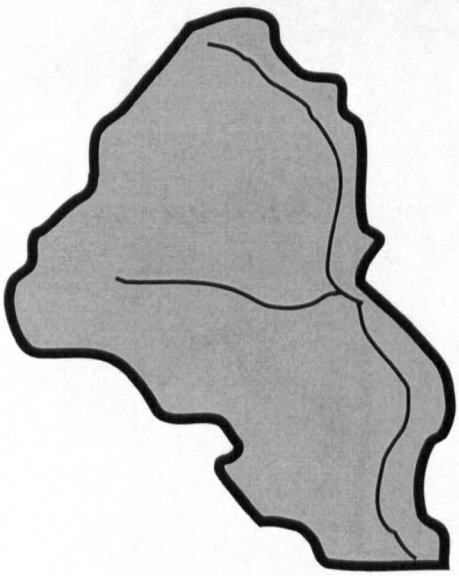
Figure A.23 - Catchment characteristics of Killigton Reservoir Tributary (Site 21)



TOPOGRAPHY



GEOLOGY



SOILS

KEY:

Kirkby Moor Flags (Sil Slates)

Stagnohumic Gley

500m

Figure A.24 - Catchment characteristics of River Mint Tributary (Site 22)

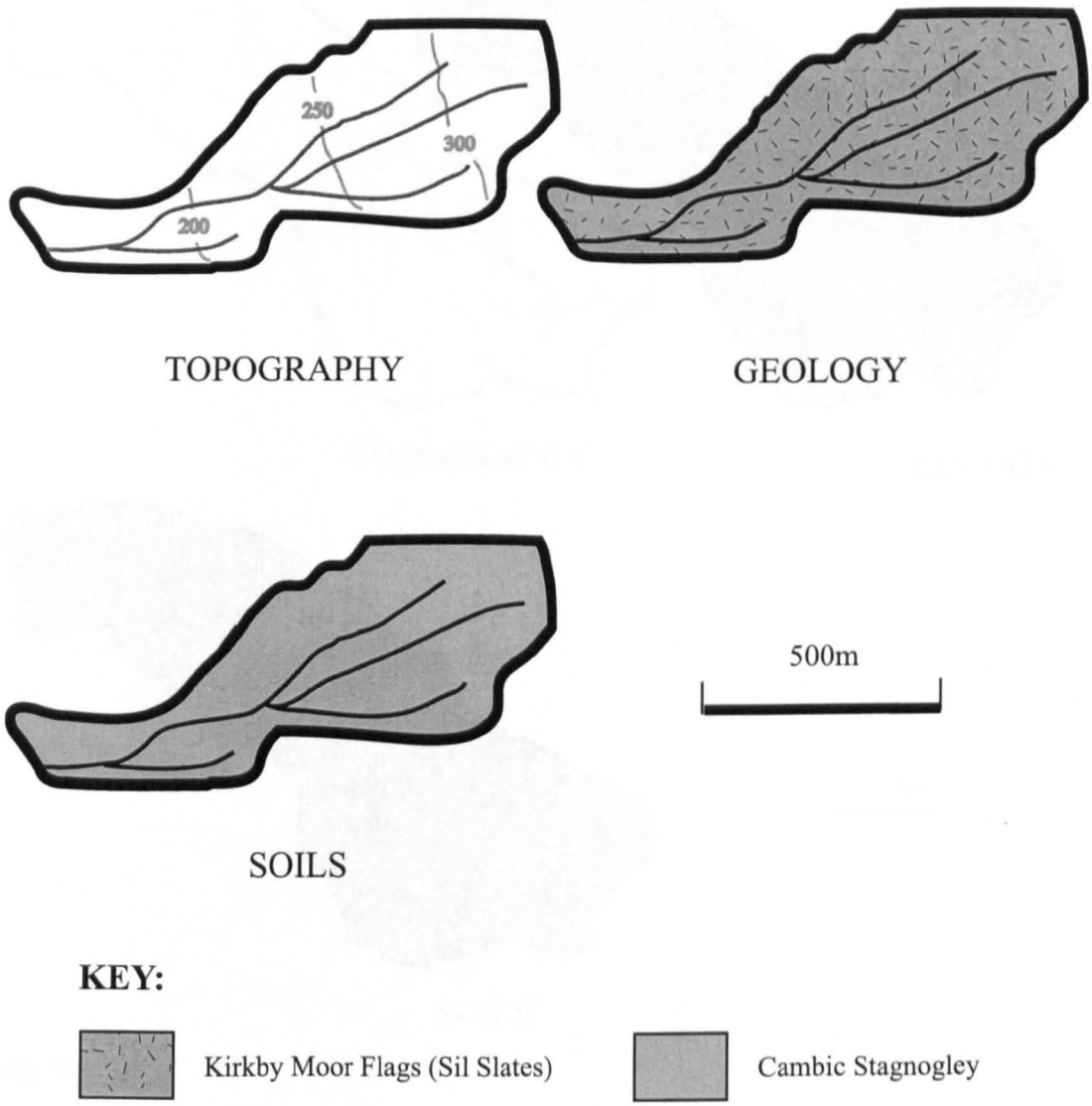
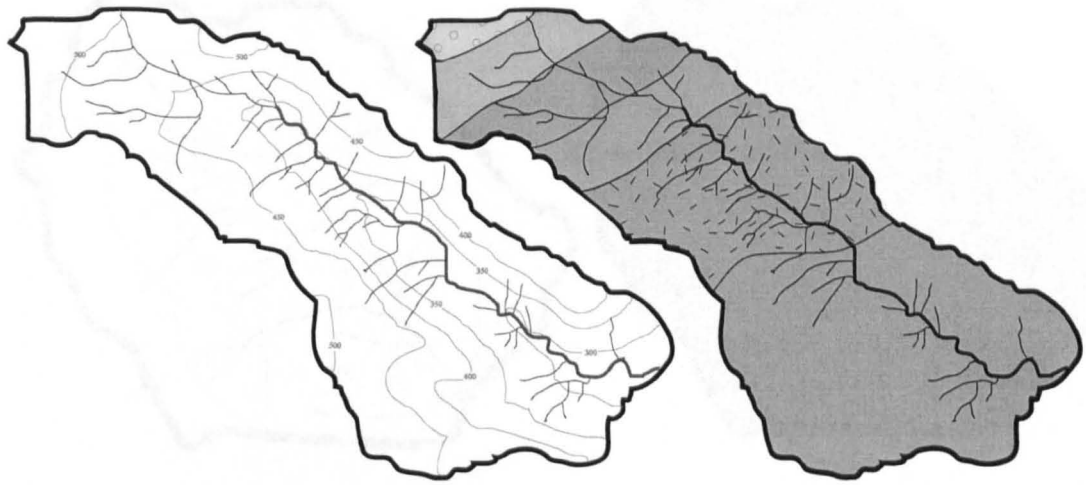
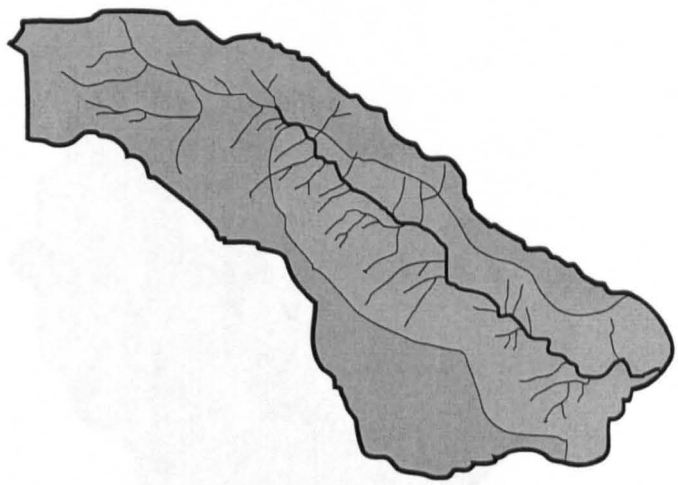


Figure A.25 - Catchment characteristics of Borrow Beck (Site 23)



TOPOGRAPHY

GEOLOGY



SOILS

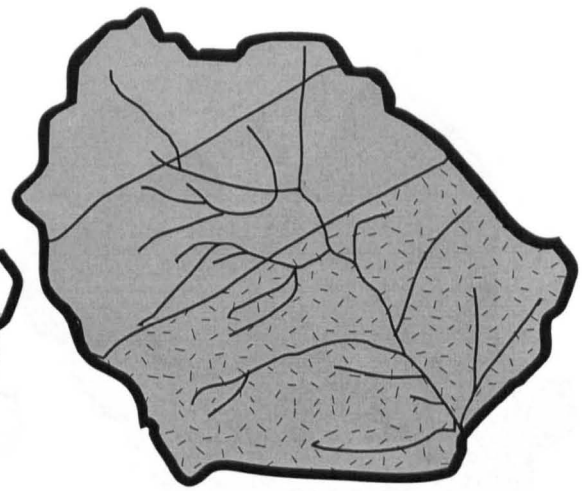
1000m

KEY:

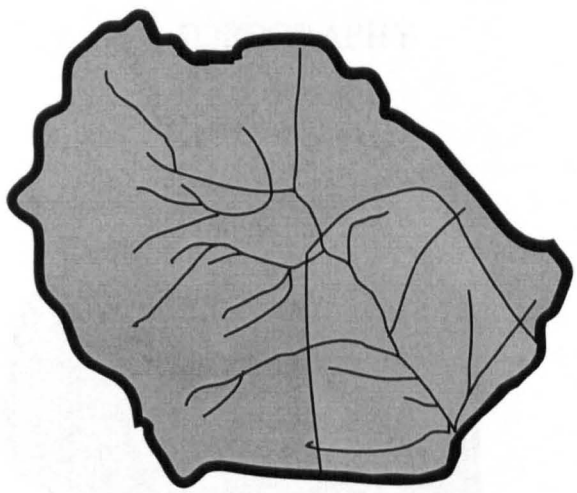
- Rhyolite (BVG)
- Con Limestone (Siurianl Slates)
- Stockdale Shale (Silurian Slates)
- Brathay Flags (Silurian Slates)
- Coniston Grits (Silurian Slates)
- Bannisdale Slates (Silurian Slates)
- Raw Oligofibrous Peat
- Typical Brown Podzol

Figure A.26 - Catchment characteristics of Bannisdale Beck (Site 24)

TOPOGRAPHY



GEOLOGY



SOILS

500m

KEY:

Kirkby Moor Flags (Sil Slates)

Brathay Flags (Sil Slates)

Bannisdale Slates (Sil Slates)

Raw Oligofibrous Peat

Ferric Stagnopodzol

Figure A.27 - Catchment characteristics of River Sprint (Site 25)

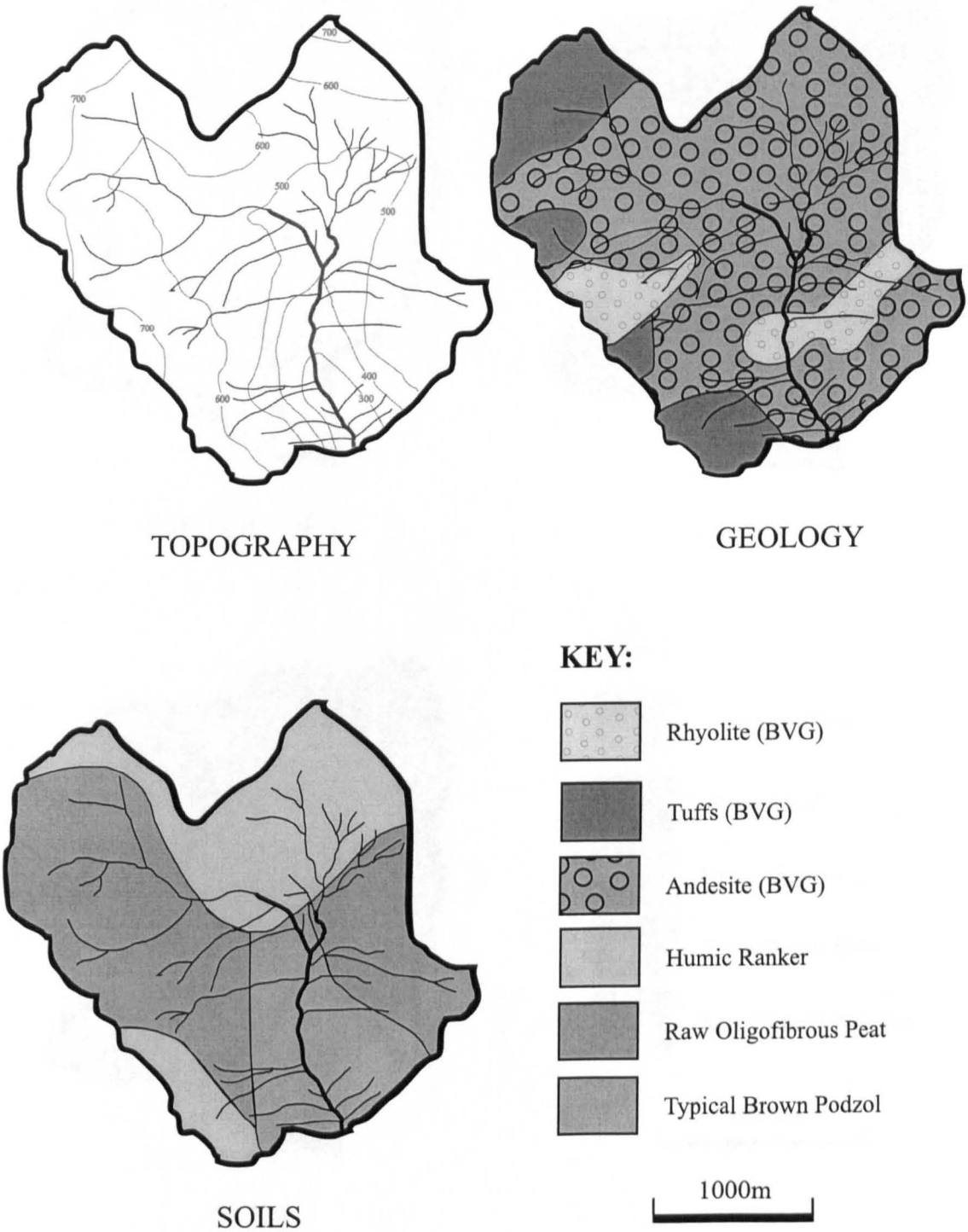
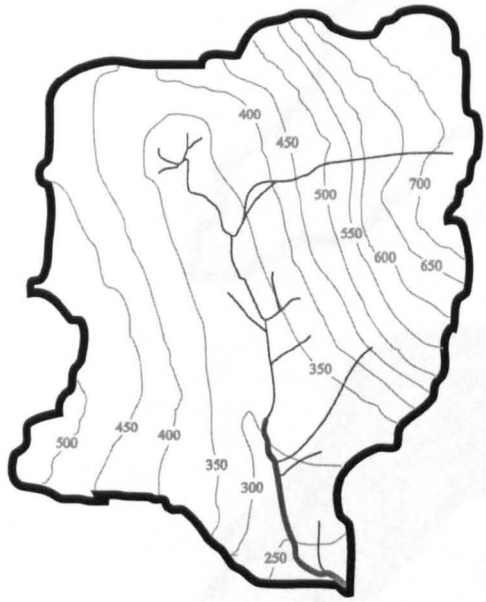


Figure A.28 - Catchment characteristics of Moasdale Beck (Site 26)



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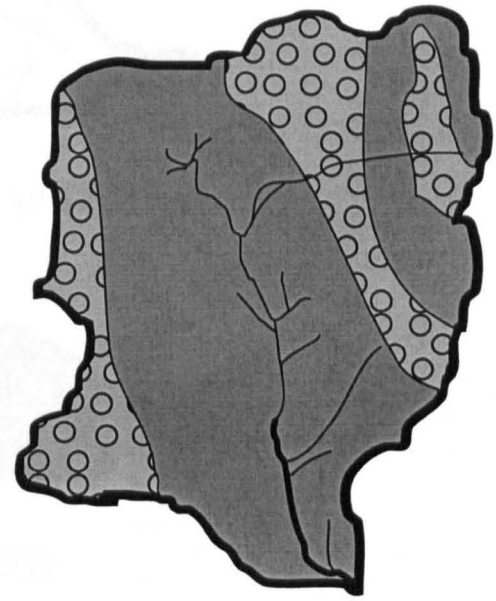
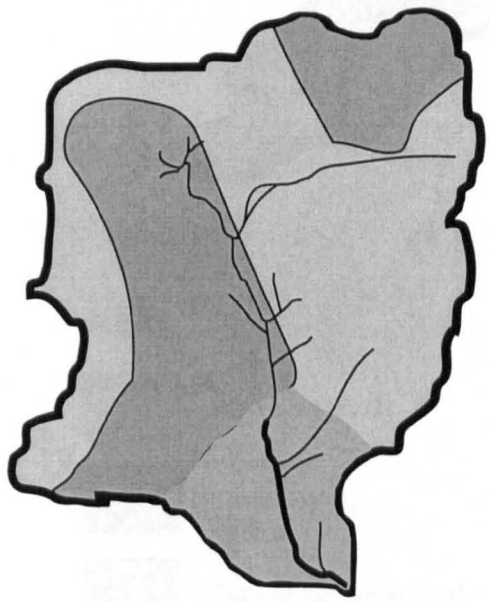


GEOLOGY



SOILS

KEY:

- Andesite (BVG)
- Tuffs (BVG)
- Humic Ranker
- Stagnohumic Gley
- Raw Oligofibrous Peat

1000m

Figure A.29 - Catchment characteristics of Castle How Beck (Site 27)

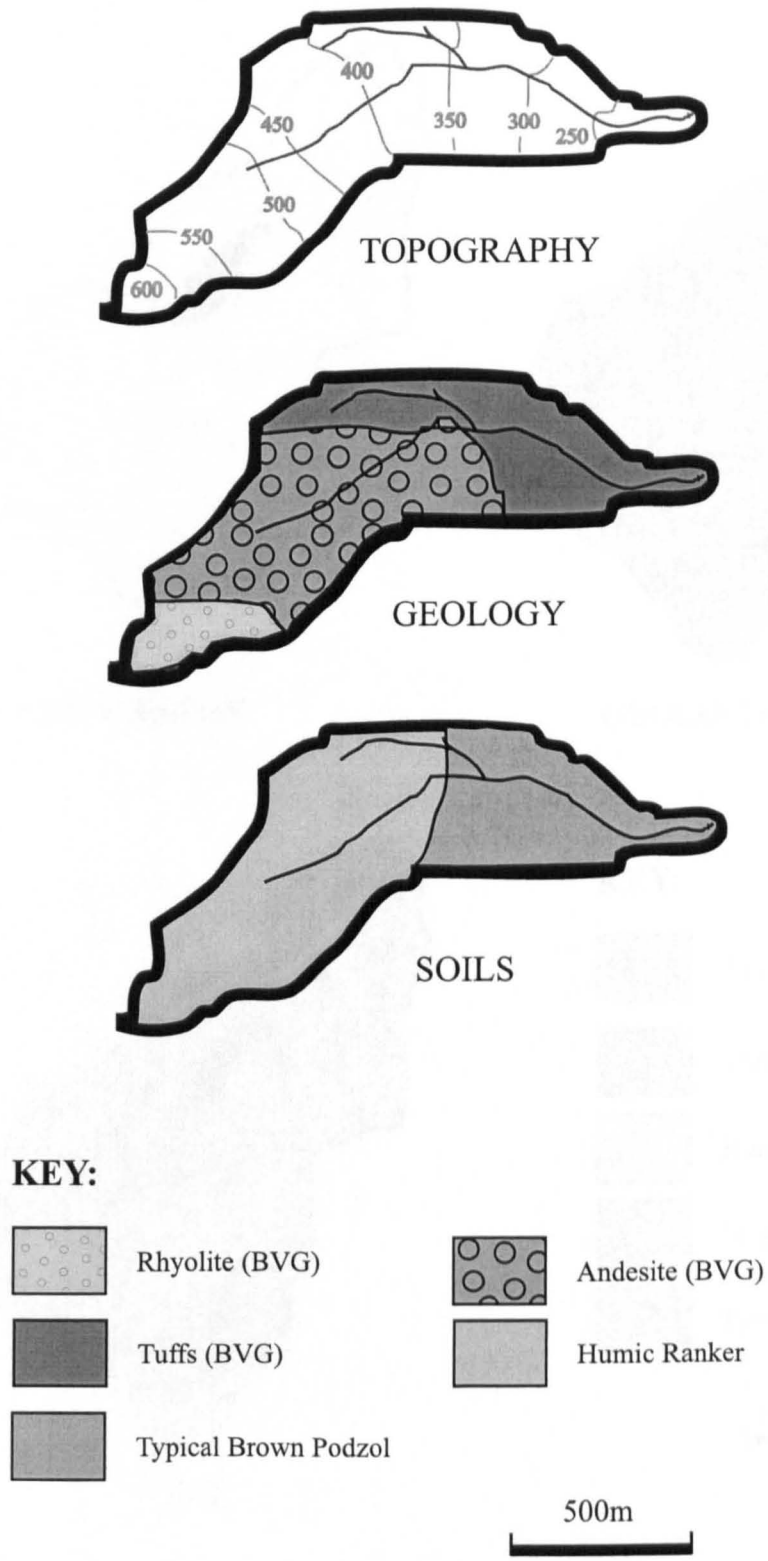
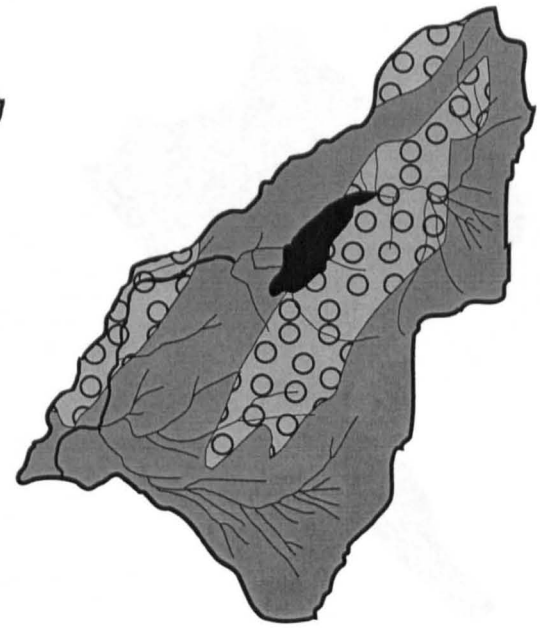
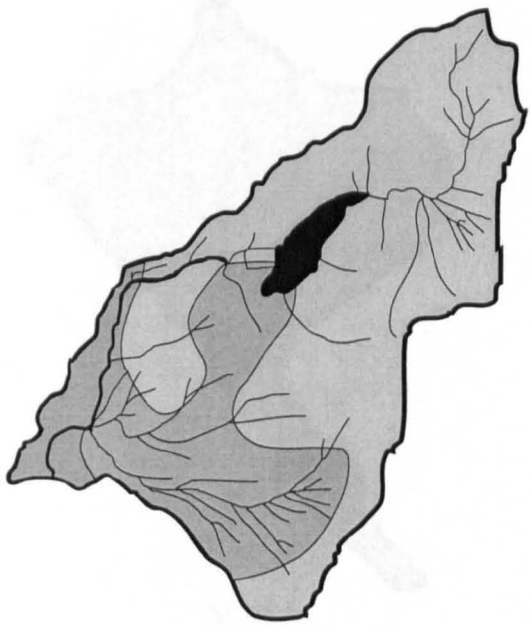


Figure A.30 - Catchment characteristics of Tarn Beck (Site 28)

TOPOGRAPHY



GEOLOGY



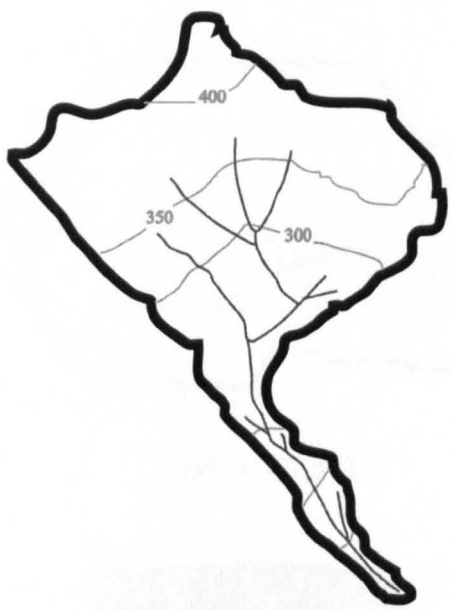
SOILS

KEY:

- Andesite (BVG)
- Tuffs (BVG)
- Humic Ranker
- Stagnohumic Gley
- Typical Brown Podzol

1000m

Figure A.31 - Catchment characteristics of Sling Beck (Site 29)



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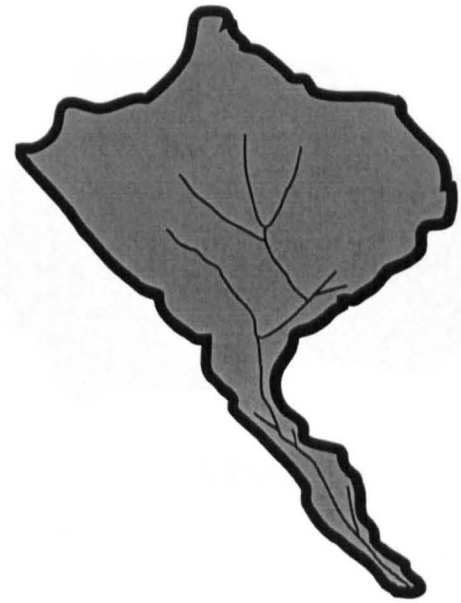


GEOLOGY

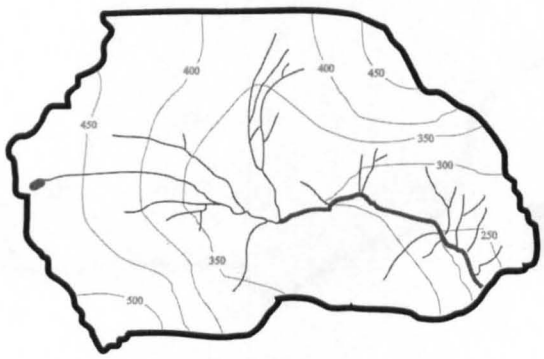
SOILS

KEY:

- Tuffs (BVG)
- Humic Ranker
- Typical Brown Podzol
- Stagnohumic Gley
- Raw Oligofibrous Peat

500m

Figure A.32 - Catchment characteristics of Holehouse Gill (Site 30)



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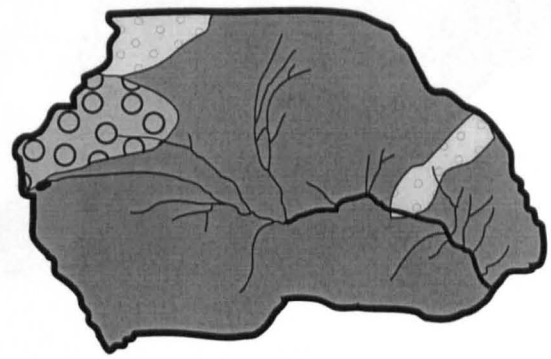

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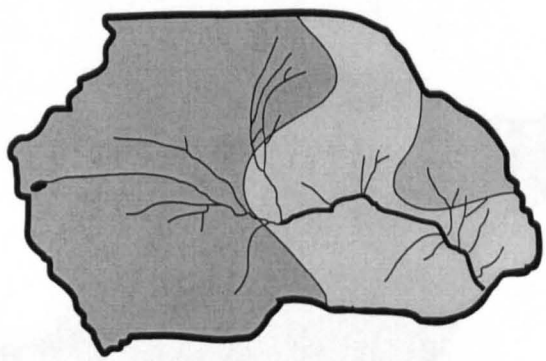


SOILS

1000m

KEY:

Rhyolite (BVG)

Andesite (BVG)

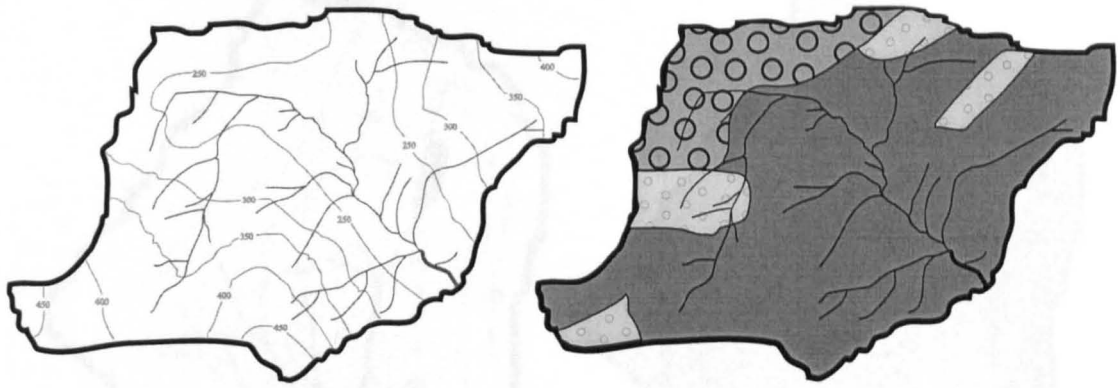
Tuffs (BVG)

Raw Oligofibrous Peat

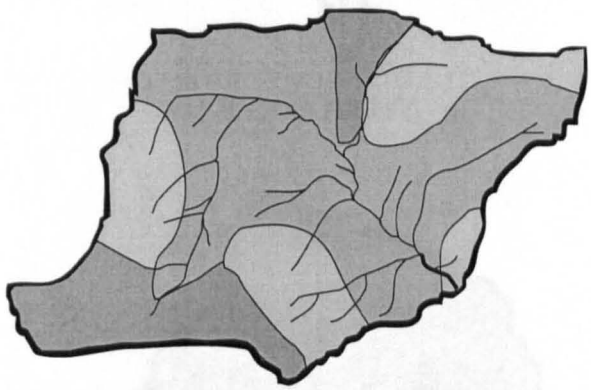
Humic Ranker

Stagnohumic Gley

Figure A.33 - Catchment characteristics of Crosby Gill (Site 31)



TOPOGRAPHY GEOLOGY



SOILS

1000m

KEY:

- Rhyolite (BVG)
- Andesite (BVG)
- Tuffs (BVG)
- Raw Oligofibrous Peat
- Stagnohumic Gley
- Humic Ranker

Figure A.34 - Catchment characteristics of Greendale Gill (Site 32)

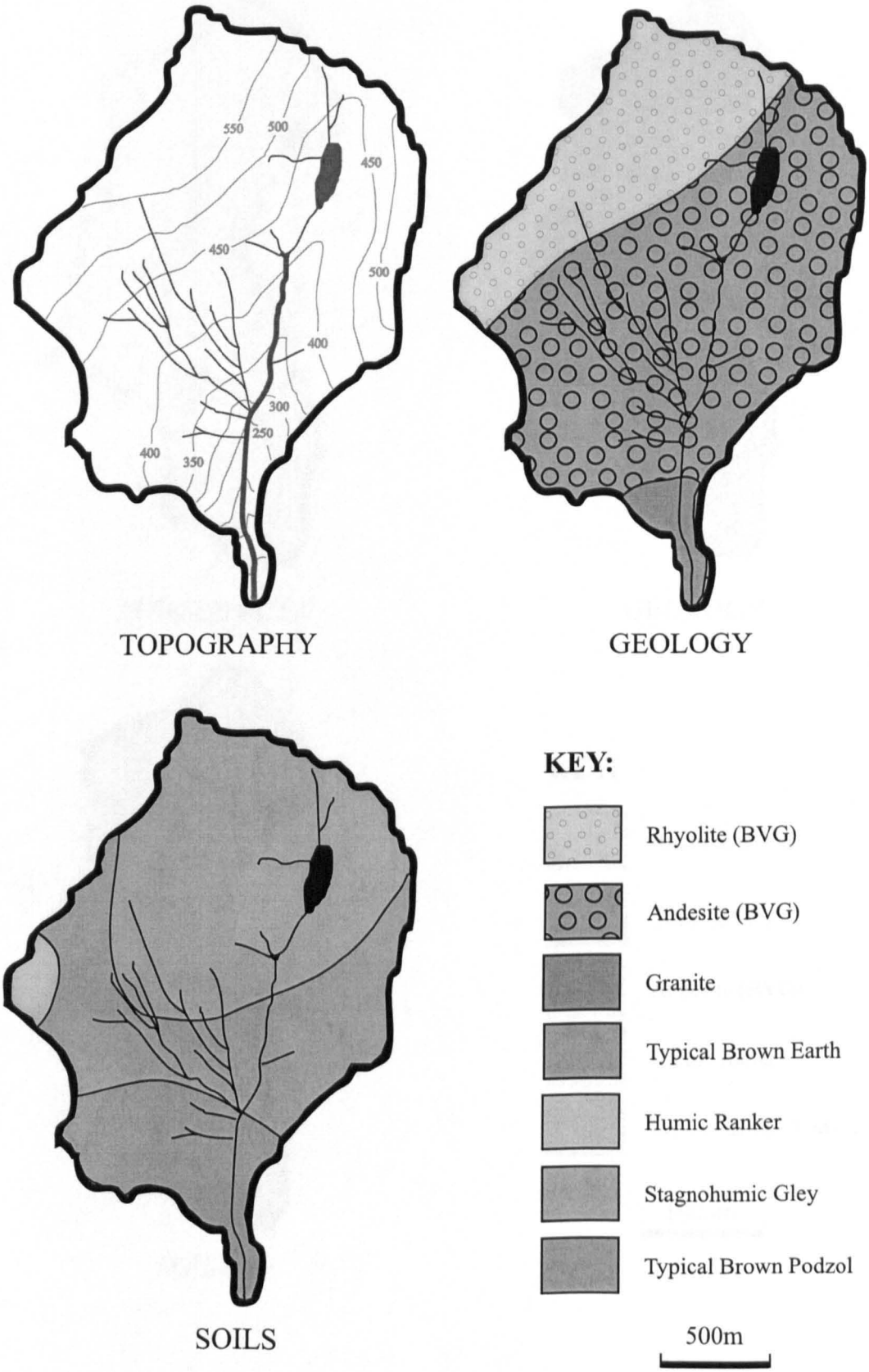


Figure A.35 - Catchment characteristics of Nether Beck (Site 33)

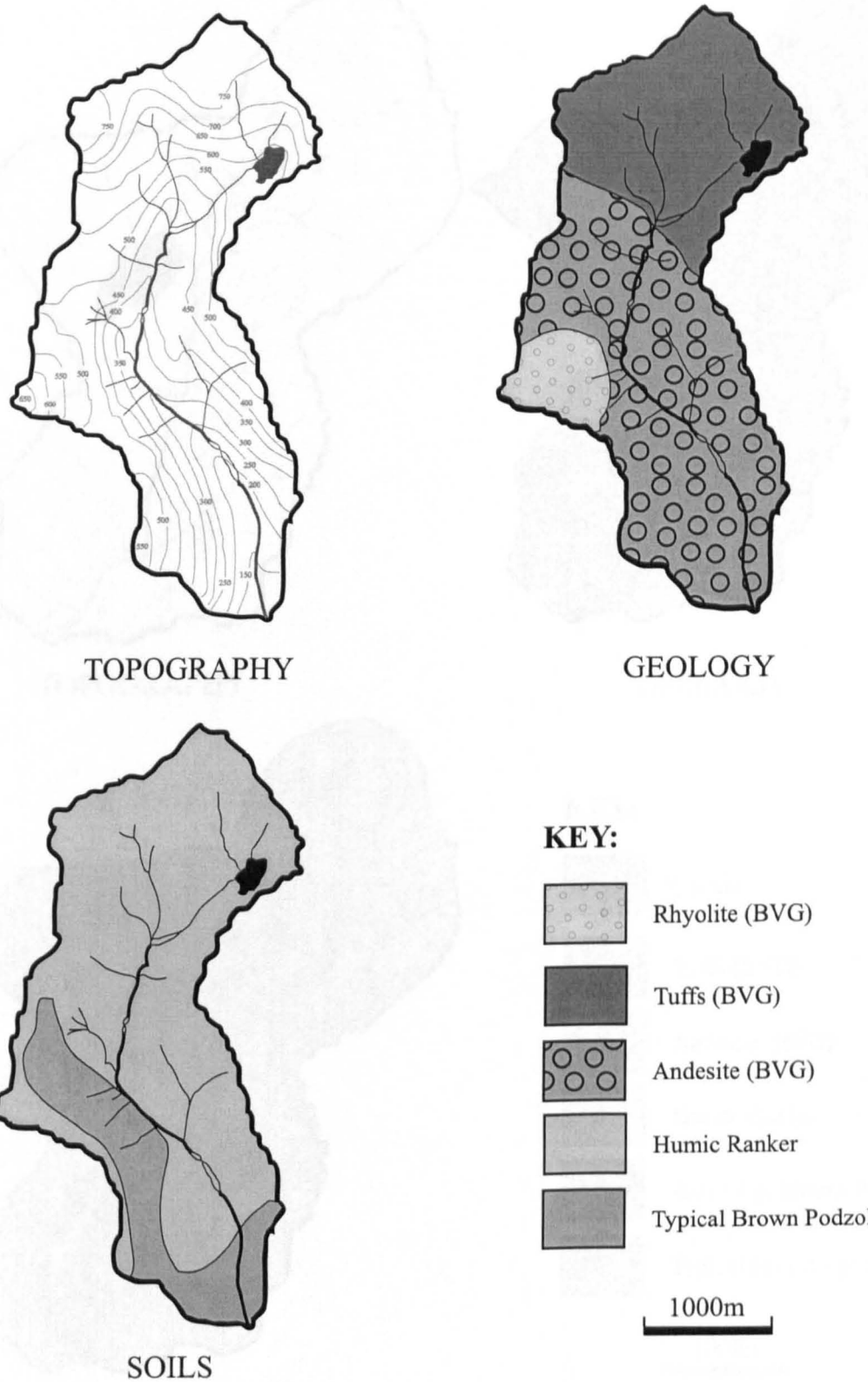


Figure A.36 - Catchment characteristics of Whillan Beck (Site 34)

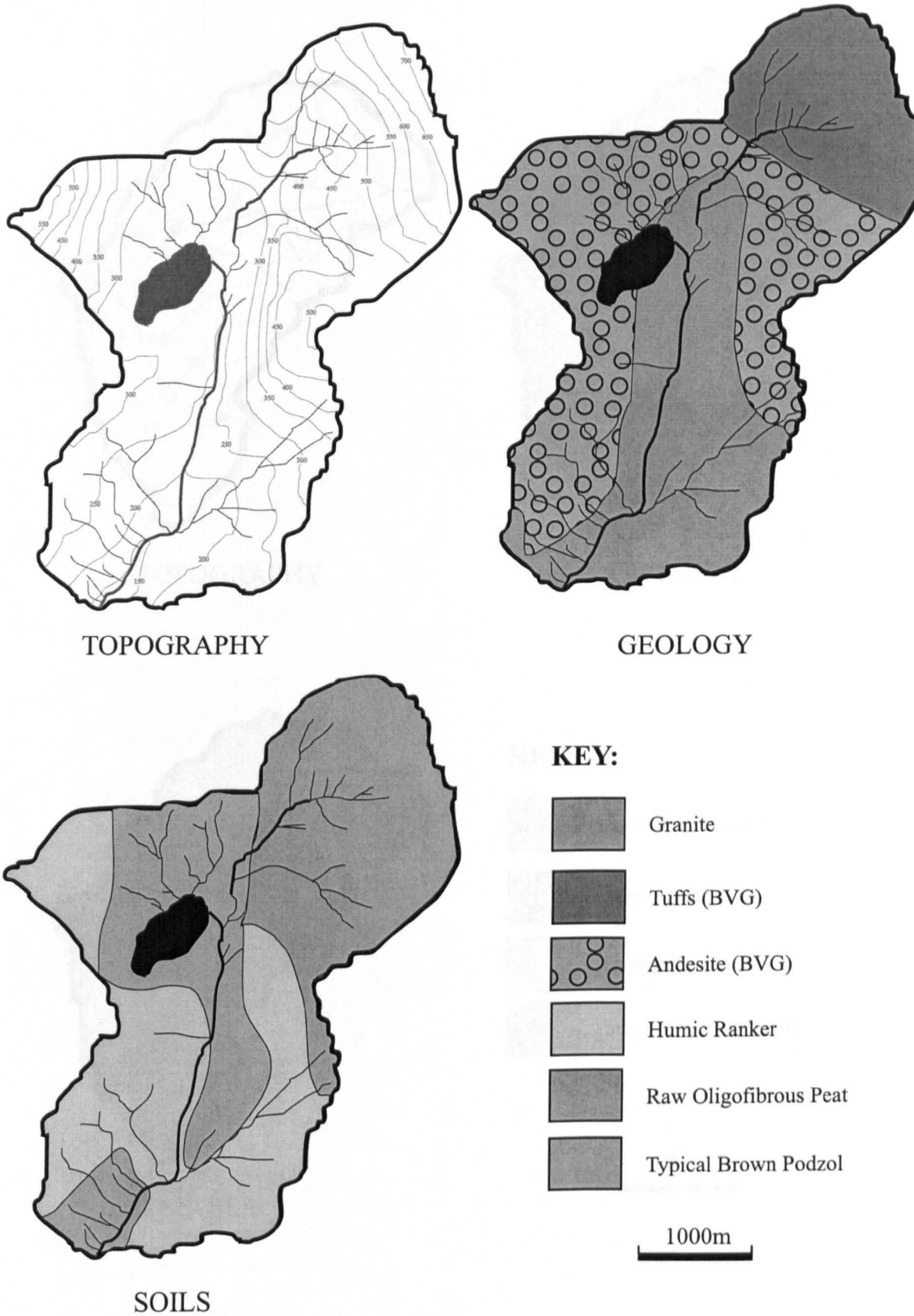


Figure A.37 - Catchment characteristics of Hardknott Gill (Site 35)

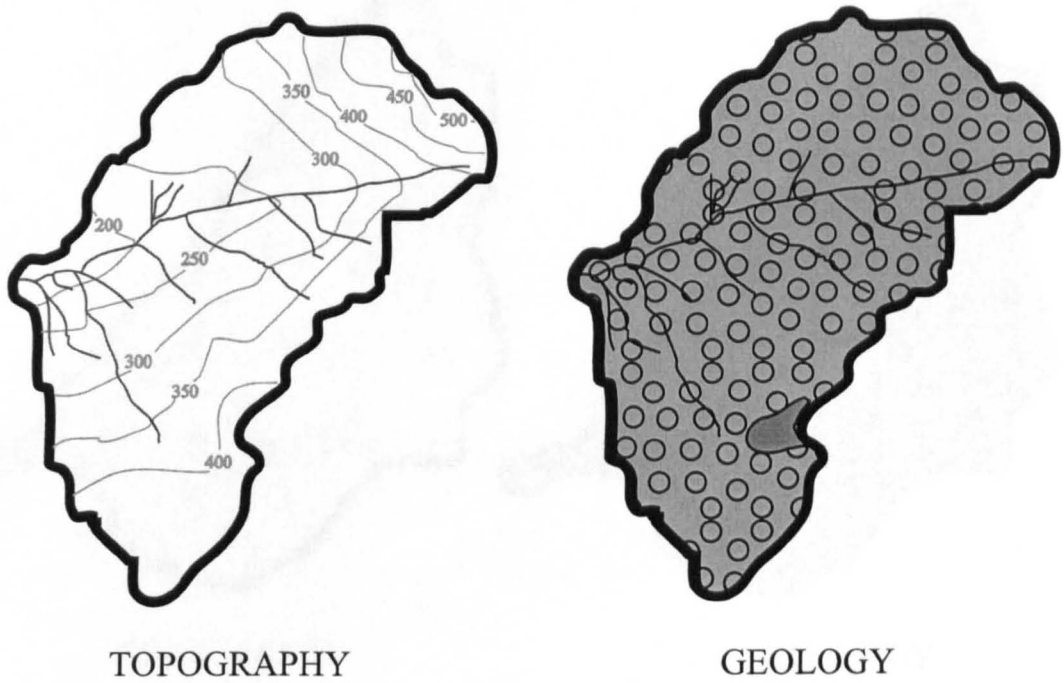
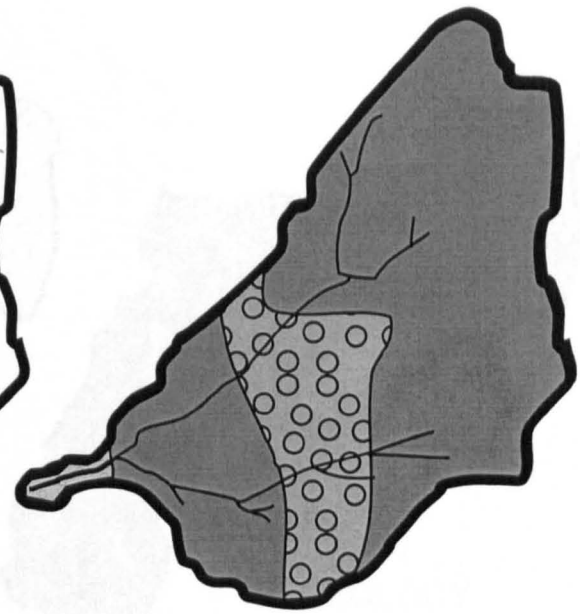
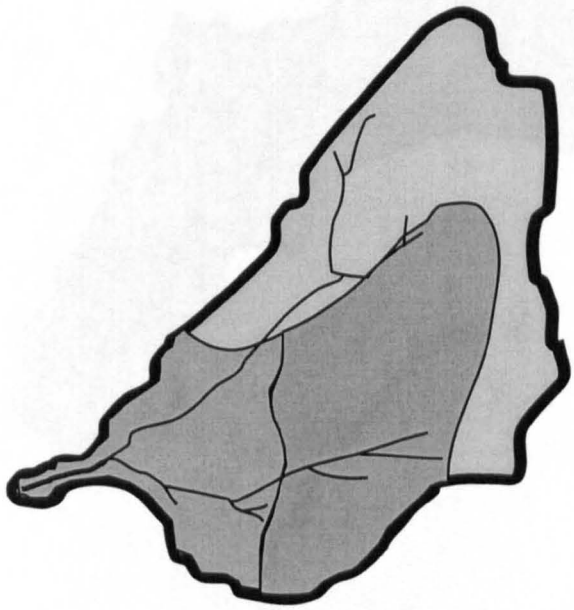


Figure A.38 - Catchment characteristics of Whelpside Ghyll (Site 36)

TOPOGRAPHY



GEOLOGY



SOILS

KEY:

- Rhyolite (BVG)
- Tuffs (BVG)
- Andesite (BVG)
- Humic Ranker
- Raw Oligofibrous Peat
- Typical Brown Podzol

500m

Figure A.39 - Catchment characteristics of Wyth Burn (Site 37)

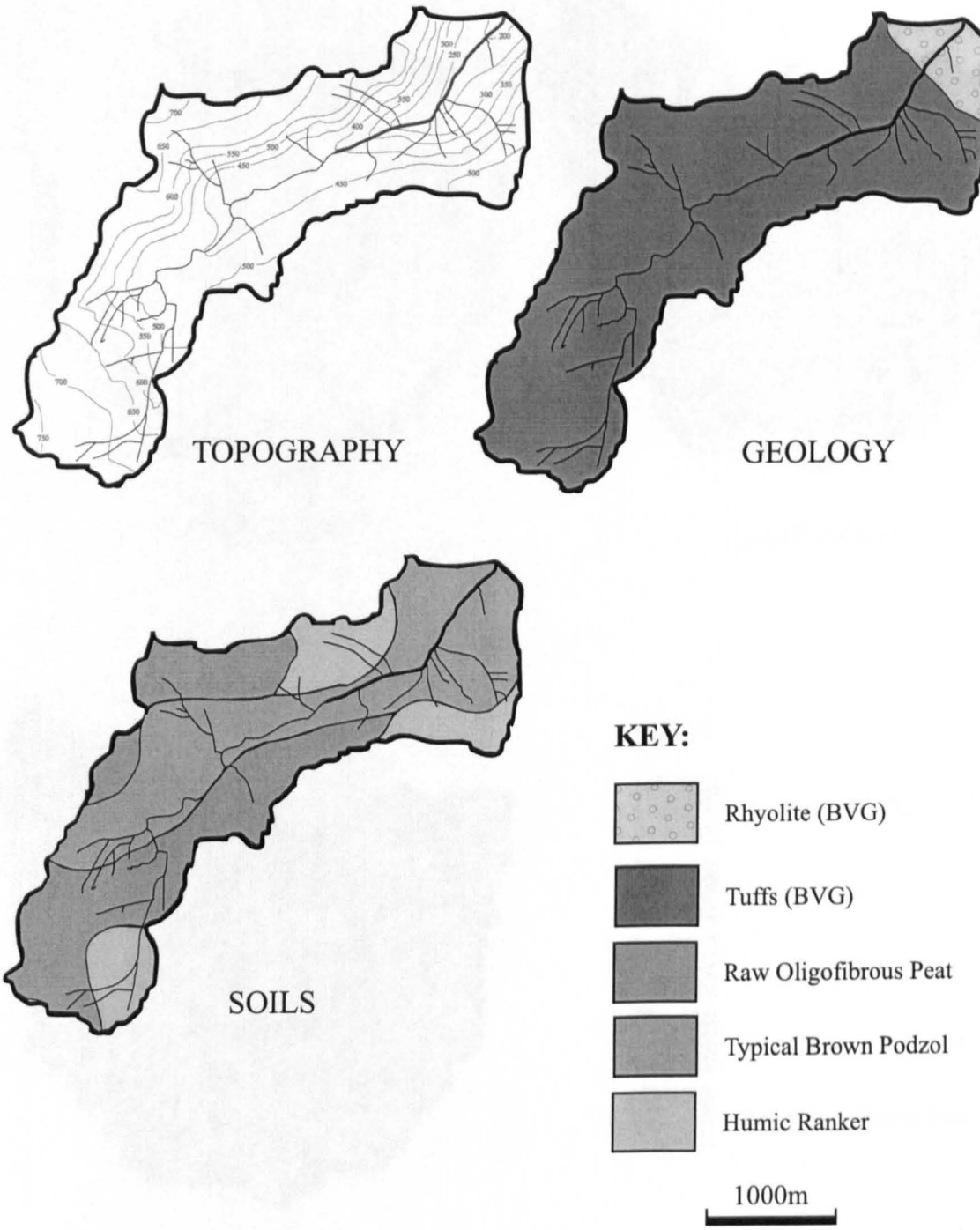


Figure A.40 - Catchment characteristics of Launchy Ghyll (Site 38)

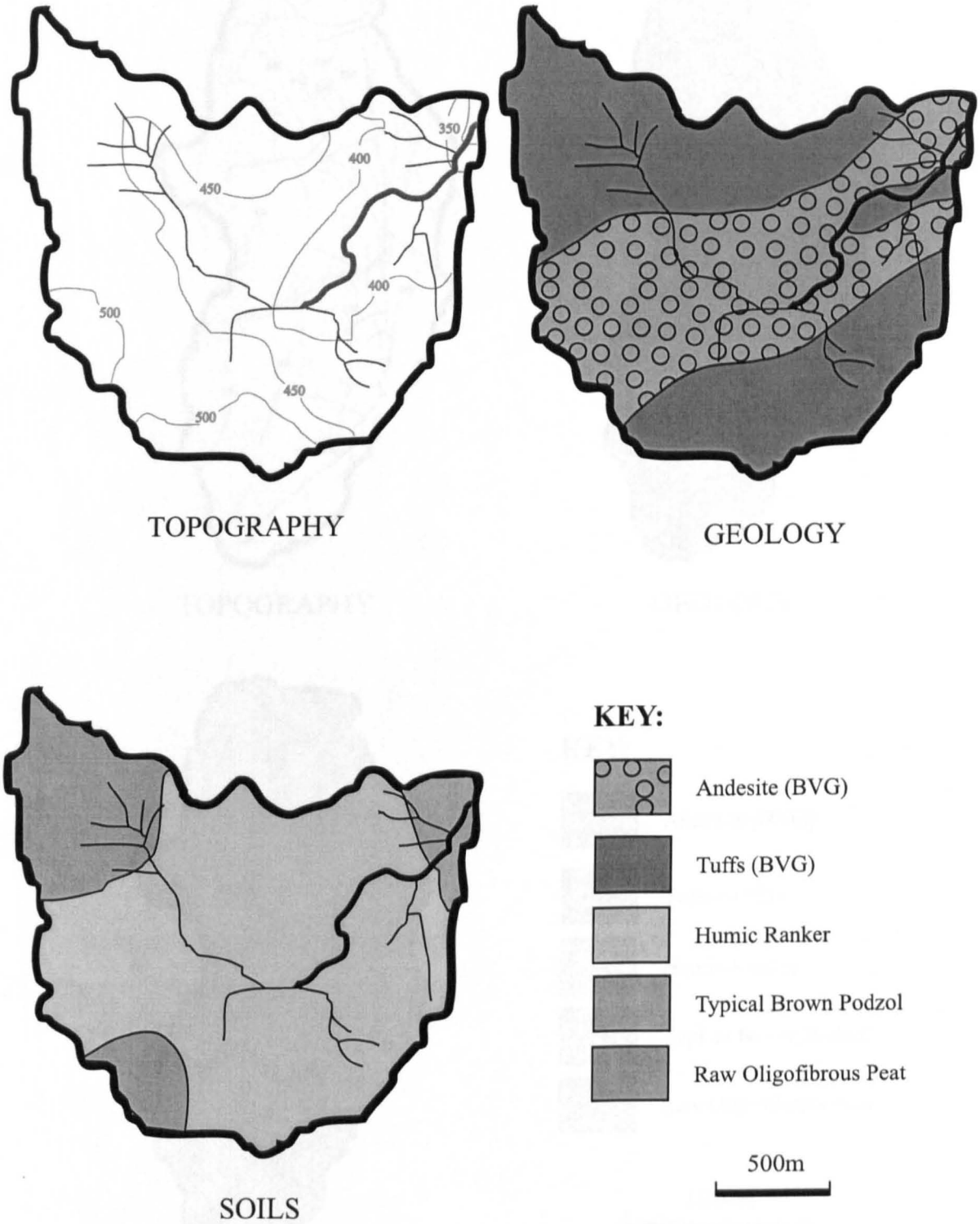
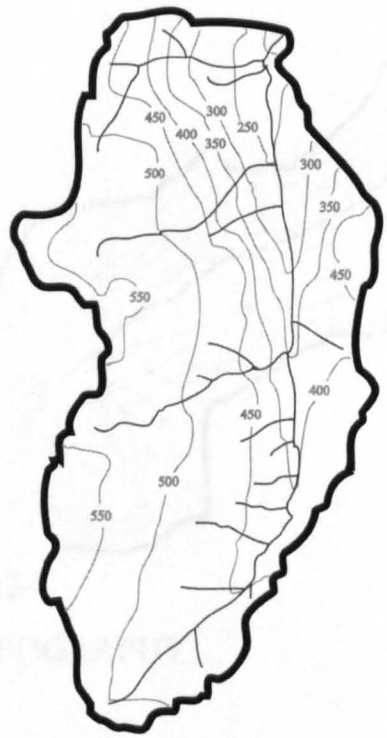


Figure A.41 - Catchment characteristics of Shoulthwaite Gill (Site 39)



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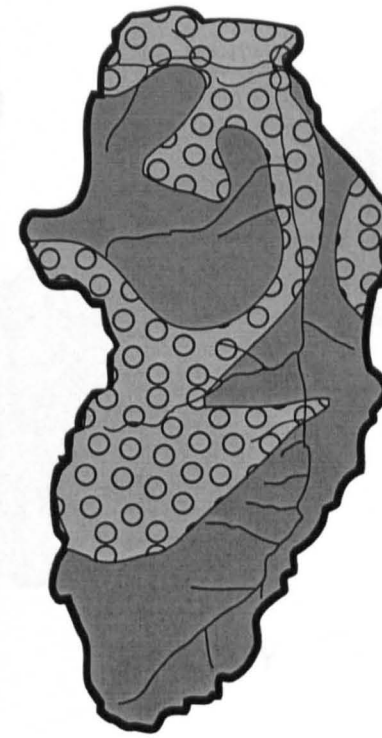
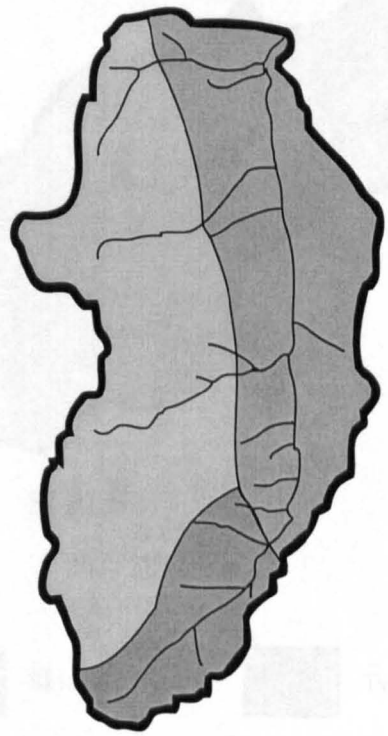


GEOLOGY



SOILS

KEY:

- Andesite (BVG)
- Tuffs (BVG)
- Humic Ranker
- Typical Brown Podzol
- Raw Oligofibrous Peat

1000m

Figure A.42 - Catchment characteristics of Coledale Beck (Site 40)

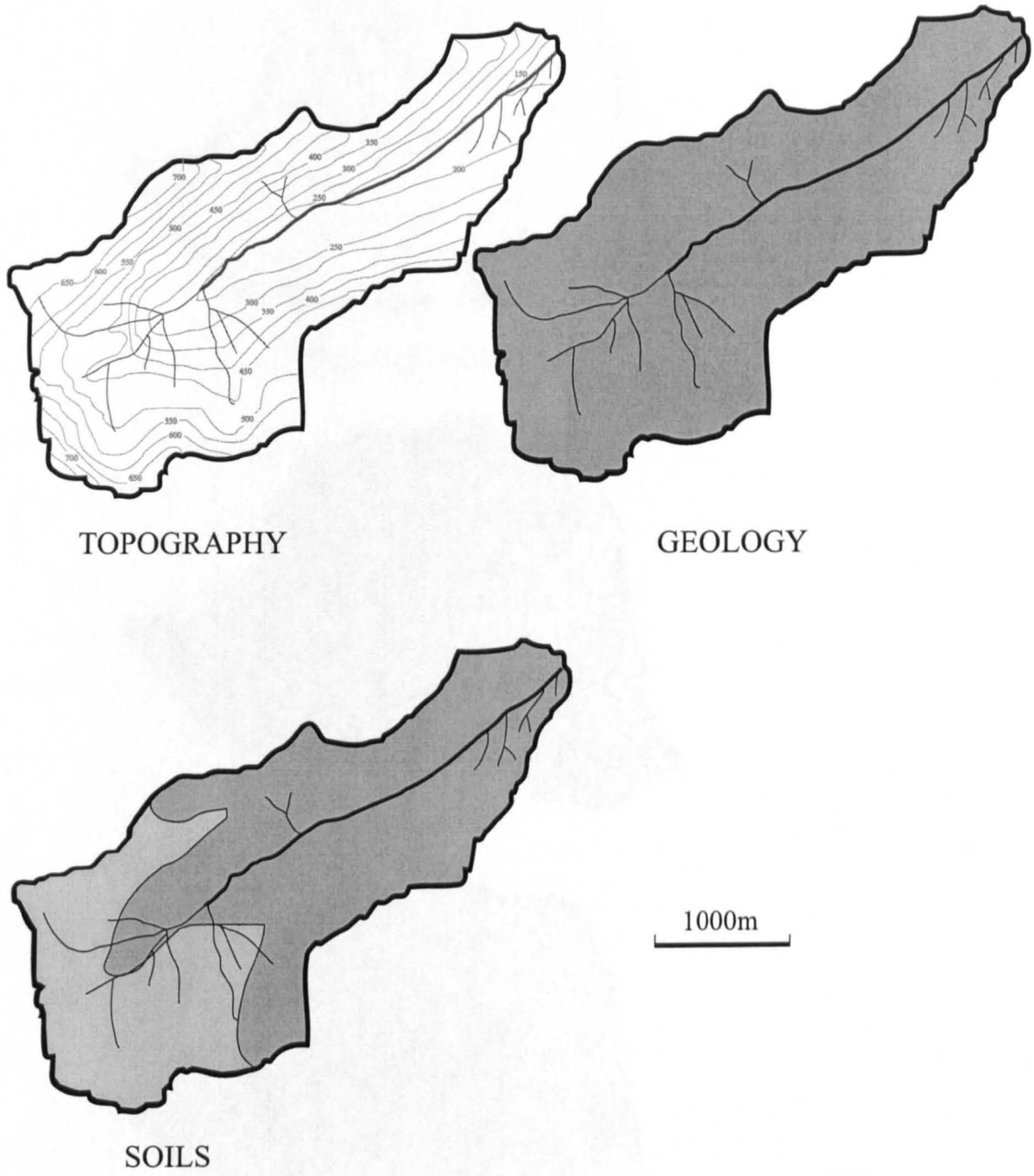


Figure A.43 - Catchment characteristics of Liza Beck (Site 41)

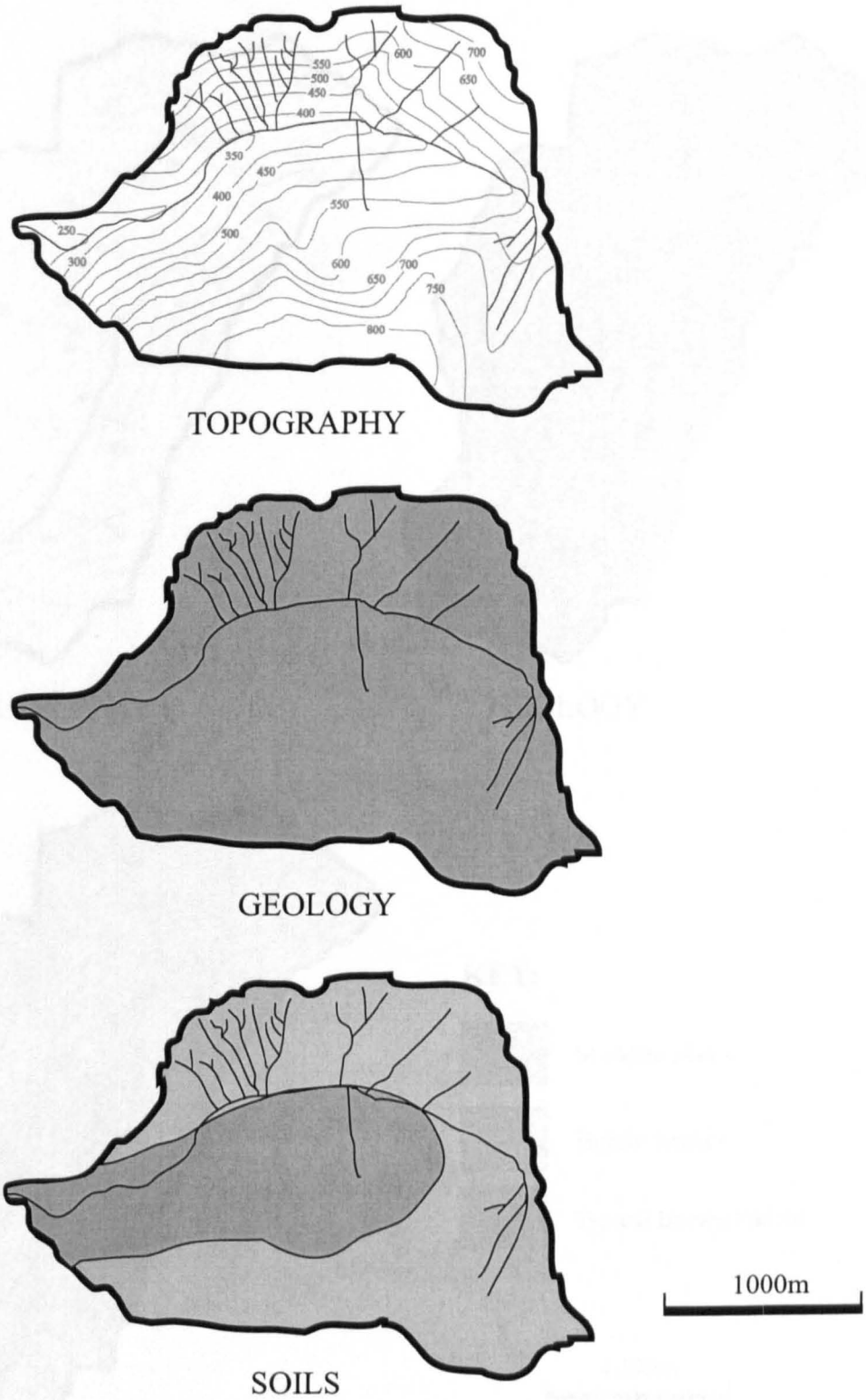
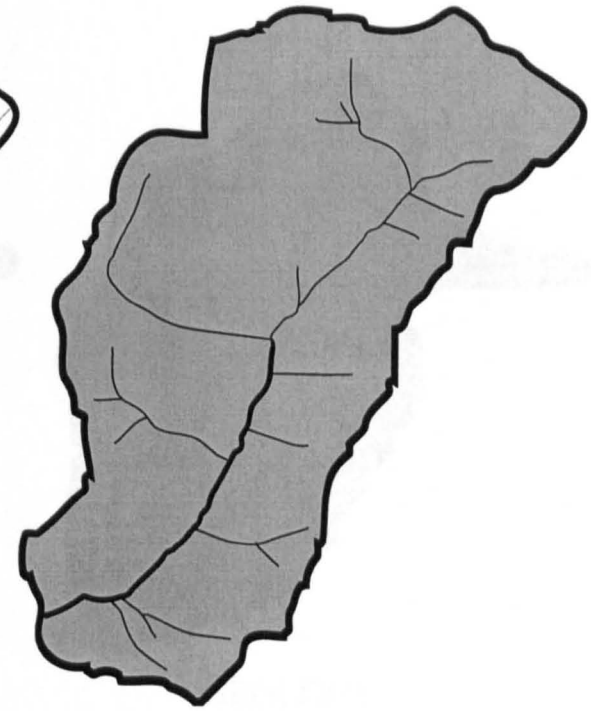


Figure A.44 - Catchment characteristics of Mill Beck 2 (Site 42)

TOPOGRAPHY



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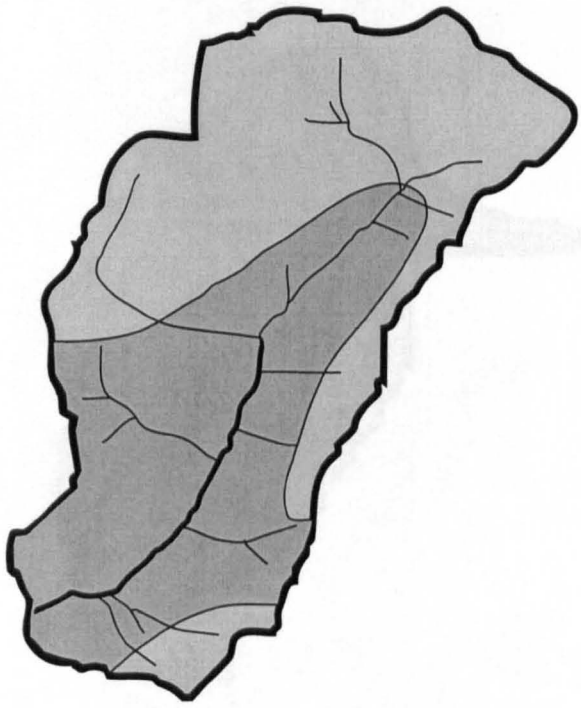


SOILS

KEY:

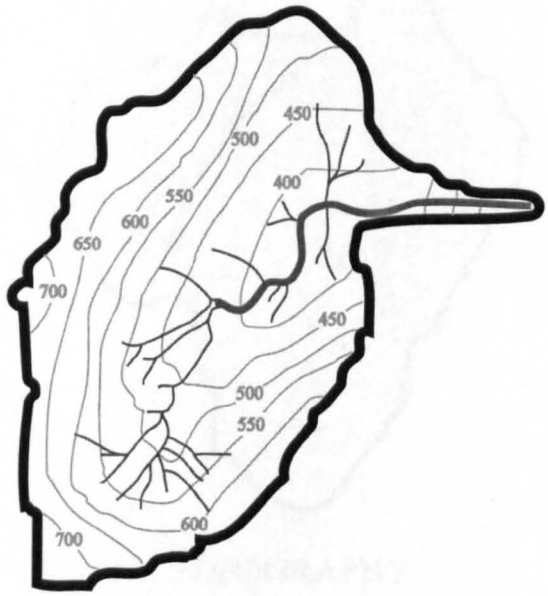
Skiddaw Slates

Humic Ranker

Typical Brown Podzol

1000m

Figure A.45 - Catchment characteristics of Sour Milk Gill (Site 43)



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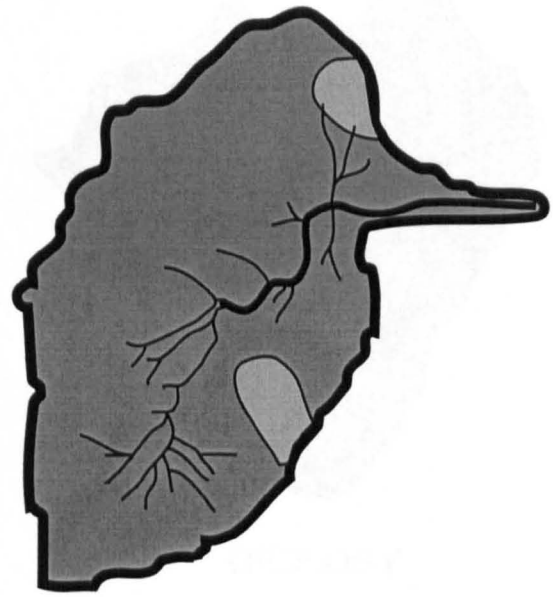

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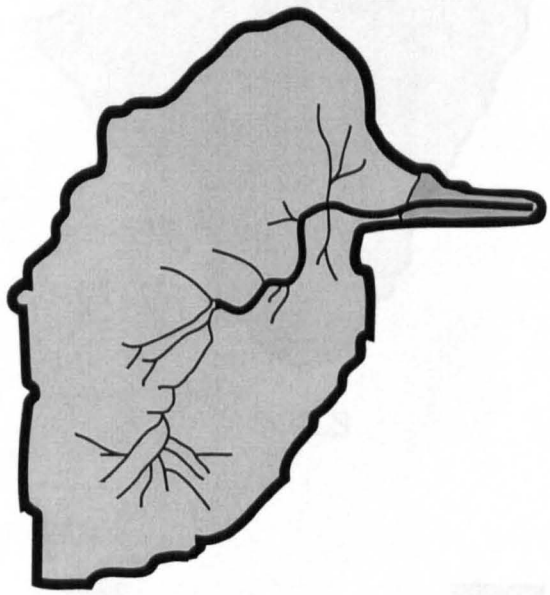


SOILS

KEY:

Tuffs (BVG)

Dolerite

Humic Ranker

Typical Brown Podzol

500m

Figure A.46 - Catchment characteristics of Styhead Gill (Site 44)

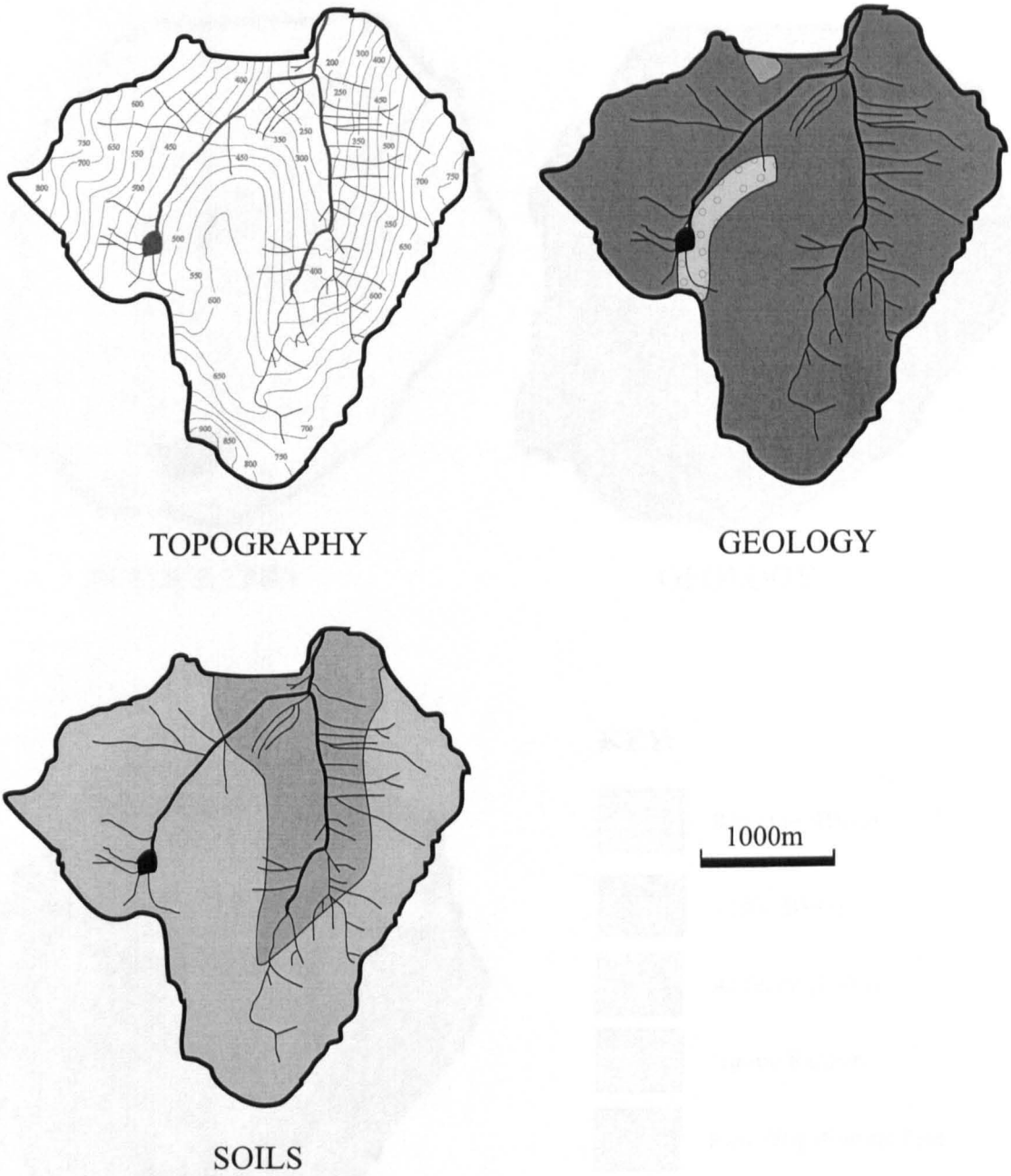
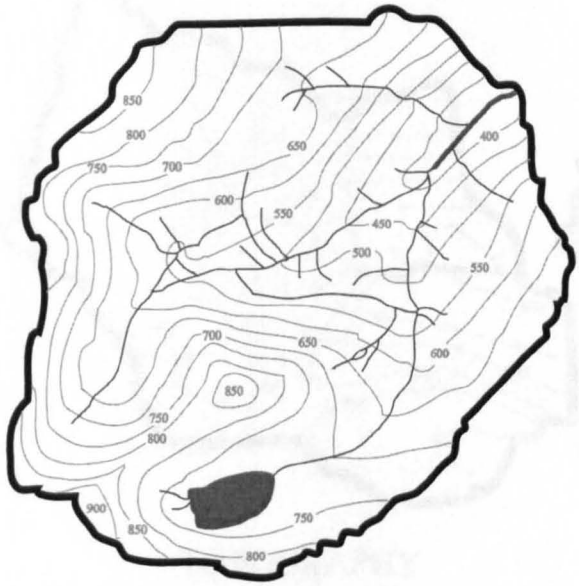


Figure A.47 - Catchment characteristics of Glenridding Beck (Site 45)



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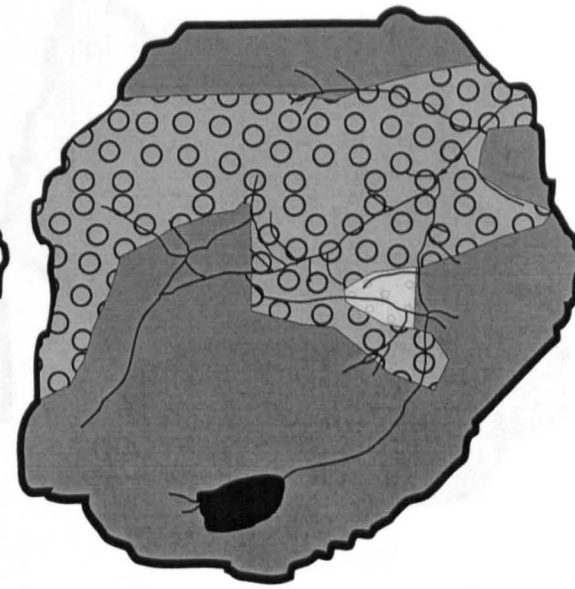
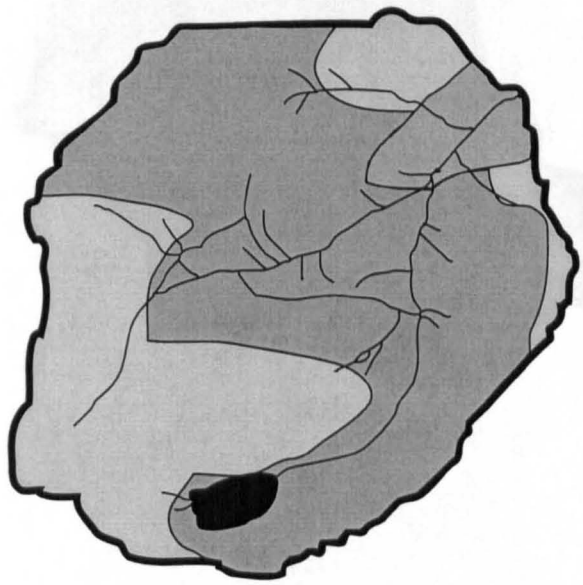


GEOLOGY



SOILS

KEY:

- Rhyolite (BVG)
- Tuffs (BVG)
- Andesite (BVG)
- Humic Ranker
- Raw Oligofibrous Peat
- Typical Brown Podzol

1000m

Figure A.48 - Catchment characteristics of Glencoyne Beck (Site 46)

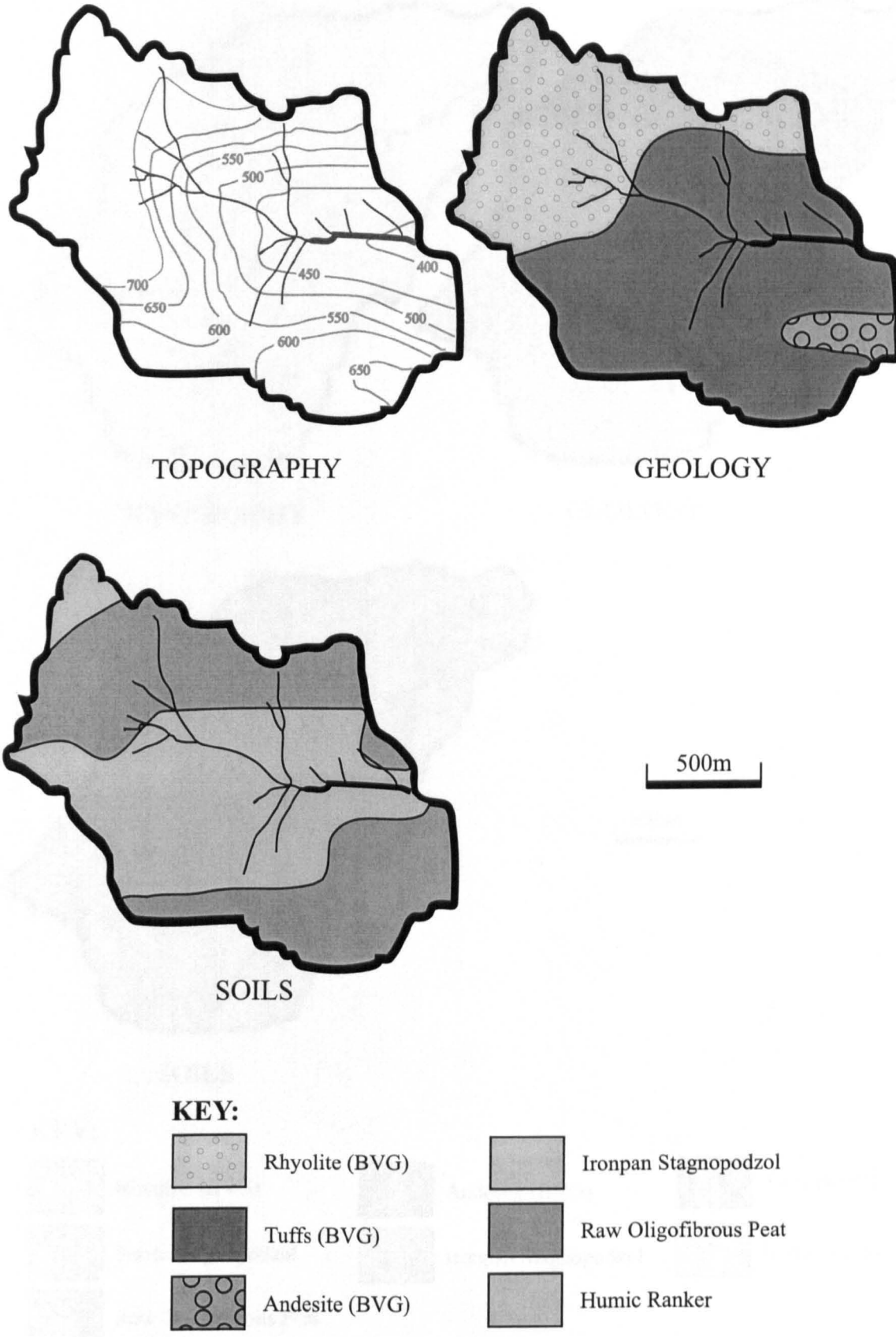
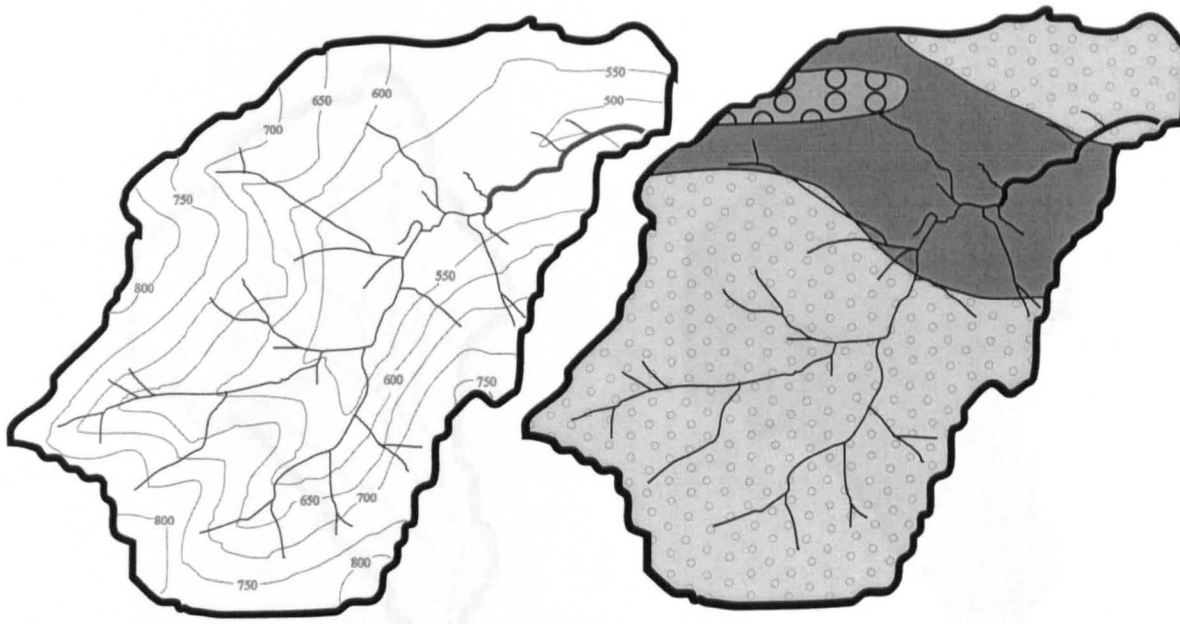
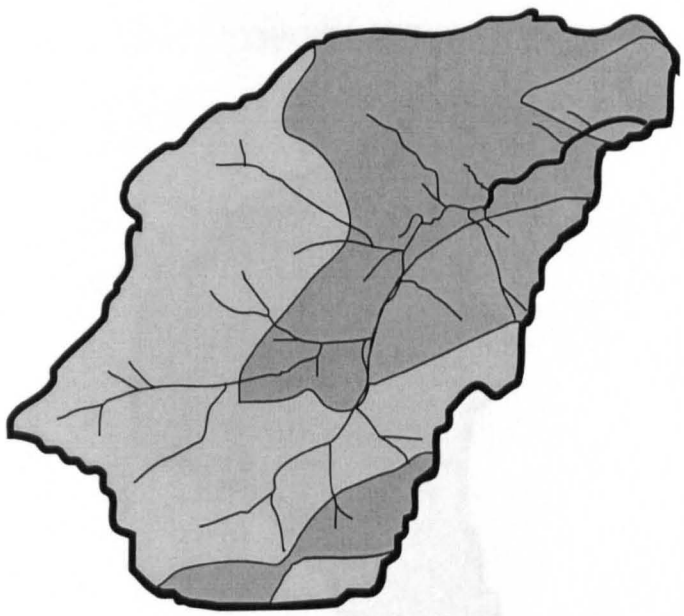


Figure A.49 - Catchment characteristics of Aira Beck (Site 47)



TOPOGRAPHY GEOLOGY



500m

SOILS

KEY:

Rhyolite (BVG)

Andesite (BVG)

Tuffs (BVG)

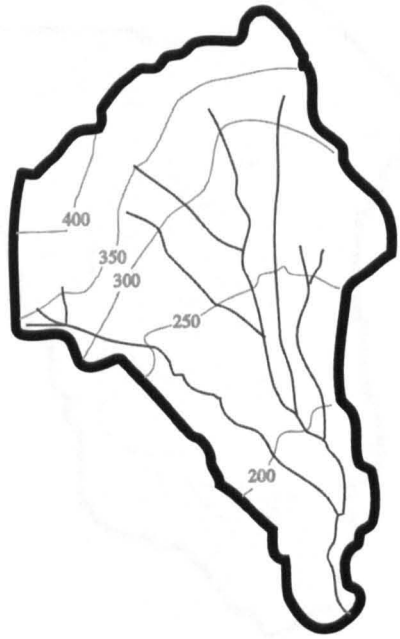
Ferric Stagnopodzol

Ironpan Stagnopodzol

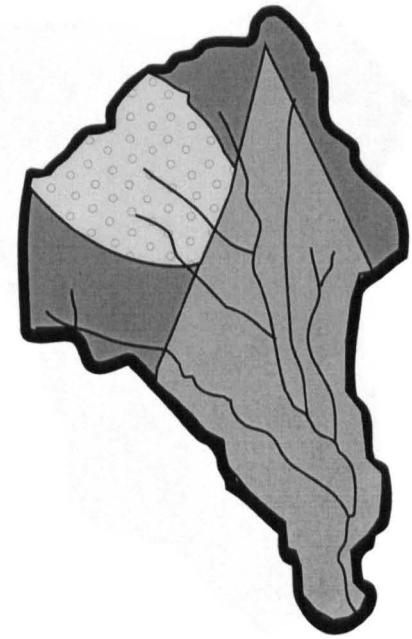
Humic Ranker

Raw Oligofibrous Peat

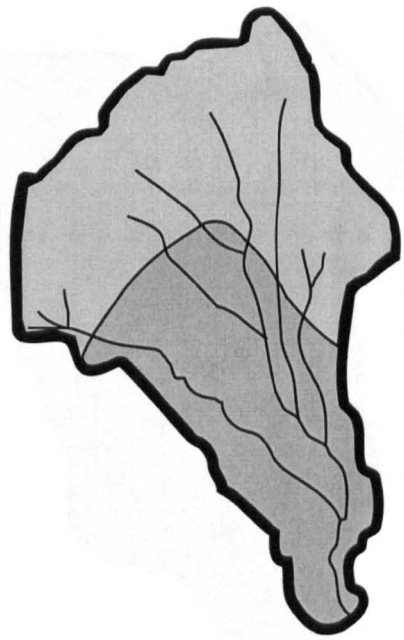
Figure A.50 - Catchment characteristics of Parkhouse Gill (Site 48)



TOPOGRAPHY



GEOLOGY



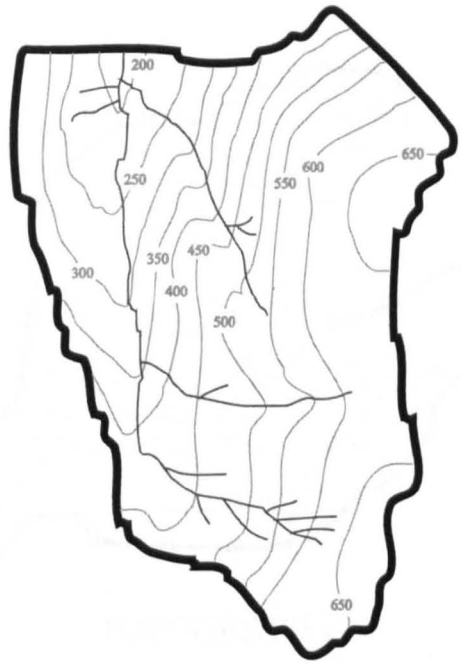
SOILS

KEY:

- Rhyolite (BVG)
- Tuffs (BVG)
- Skiddaw Slates
- Cambic Stagnogley
- Humic Ranker

500m

Figure A.51 - Catchment characteristics of Fusedale Beck (Site 49)



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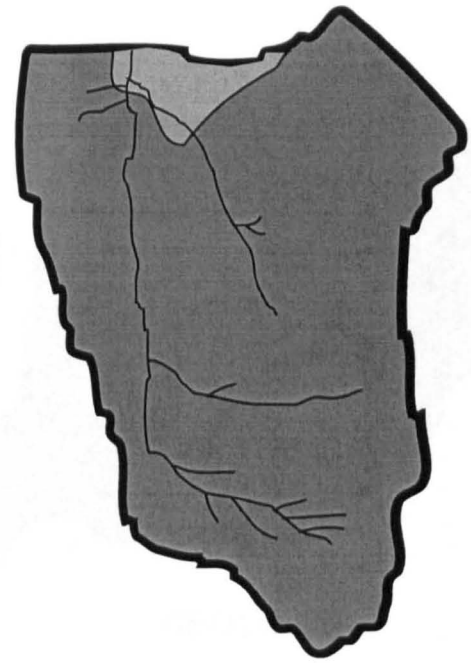

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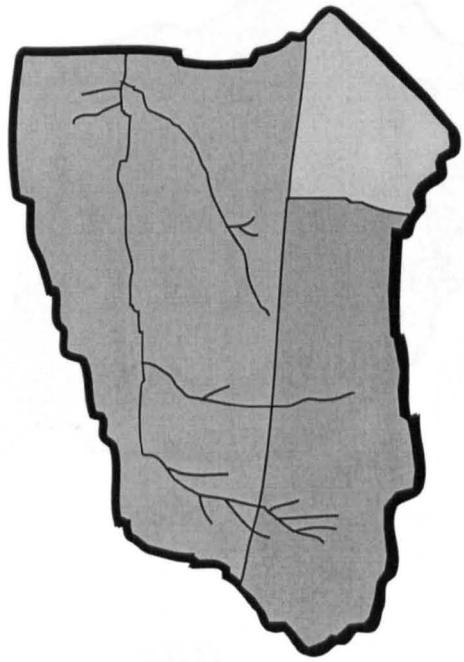


SOILS

KEY:

- Tuffs (BVG)
- Basaltic Lava
- Typical Brown Podzol
- Ironpan Stagnopodzol
- Raw Oligofibrous Peat

1000m

Figure A.52 - Catchment characteristics of Heltondale Beck (Site 50)

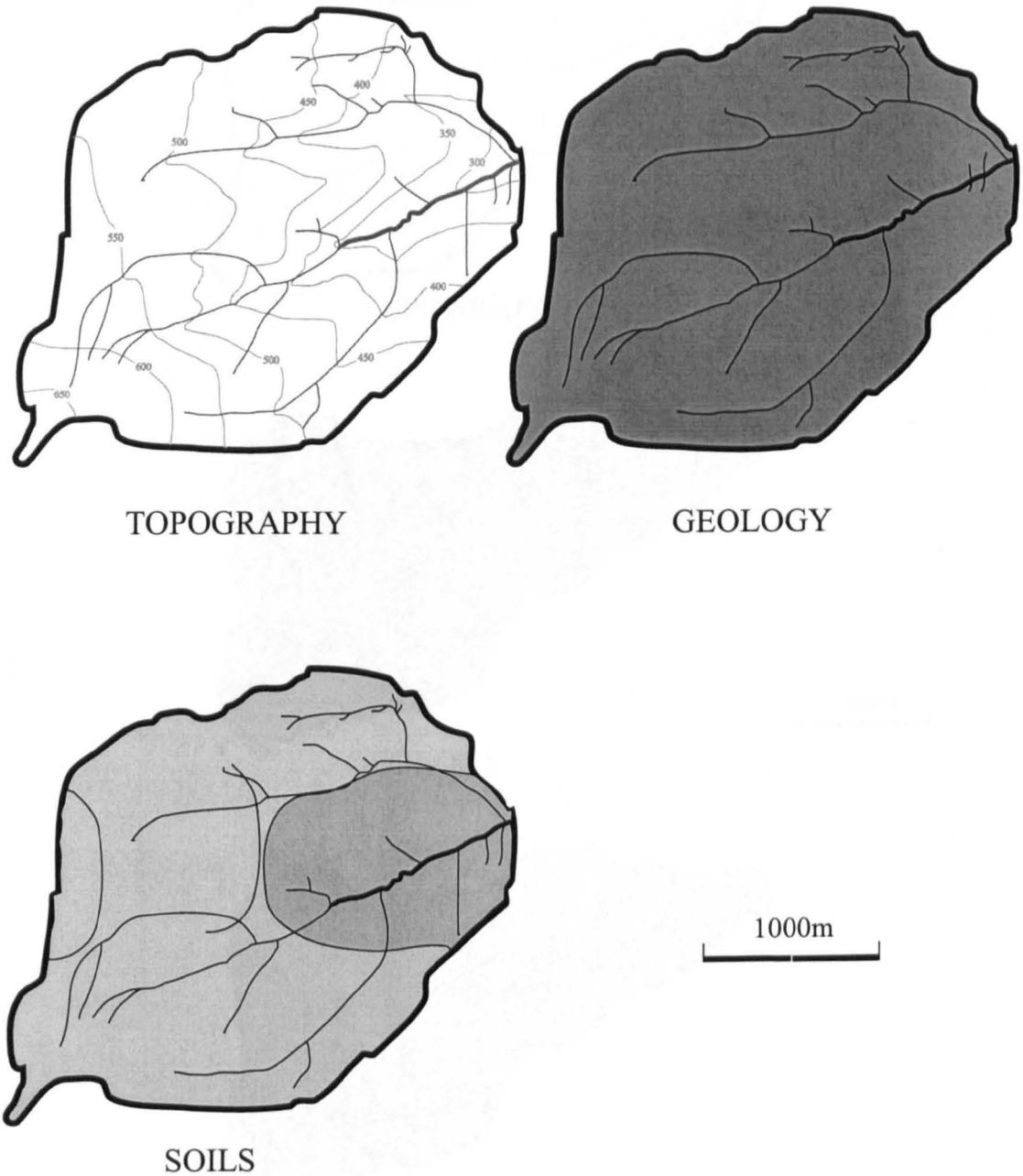
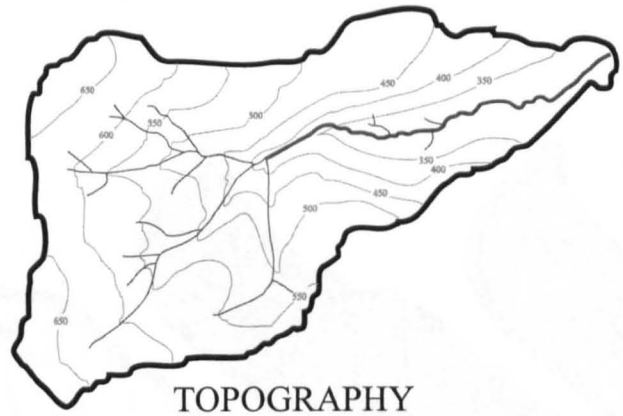


Figure A.53 - Catchment characteristics of Cawdale Beck (Site 51)



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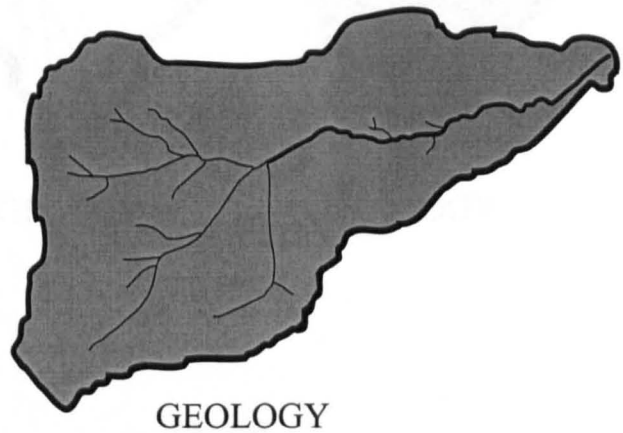
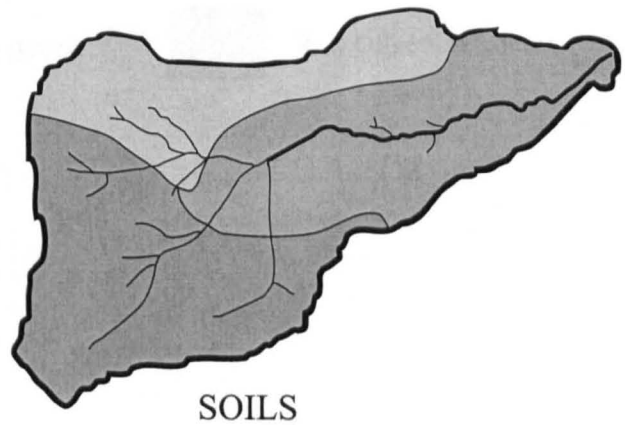


1000m

GEOLOGY

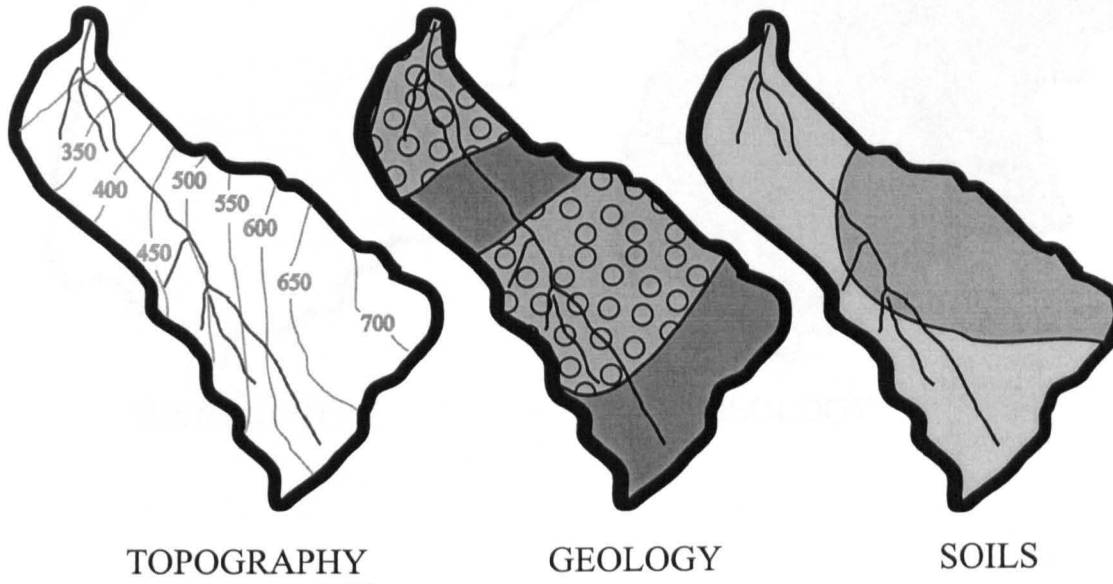


SOILS

KEY:

- Tuffs (BVG)
- Raw Oligofibrous Peat
- Typical Brown Podzol
- Ironpan Stagnopodzol

Figure A.54 - Catchment characteristics of Gatescarth Beck (Site 52)



KEY:

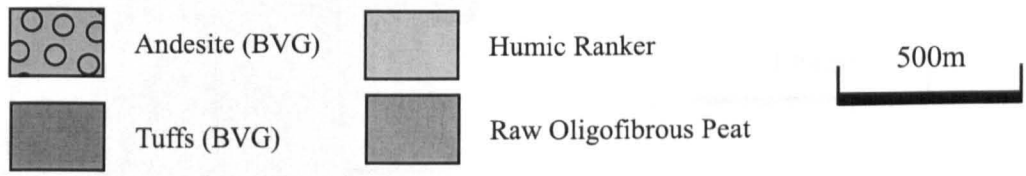


Figure A.55 - Catchment characteristics of Naddle Beck (Site 53)

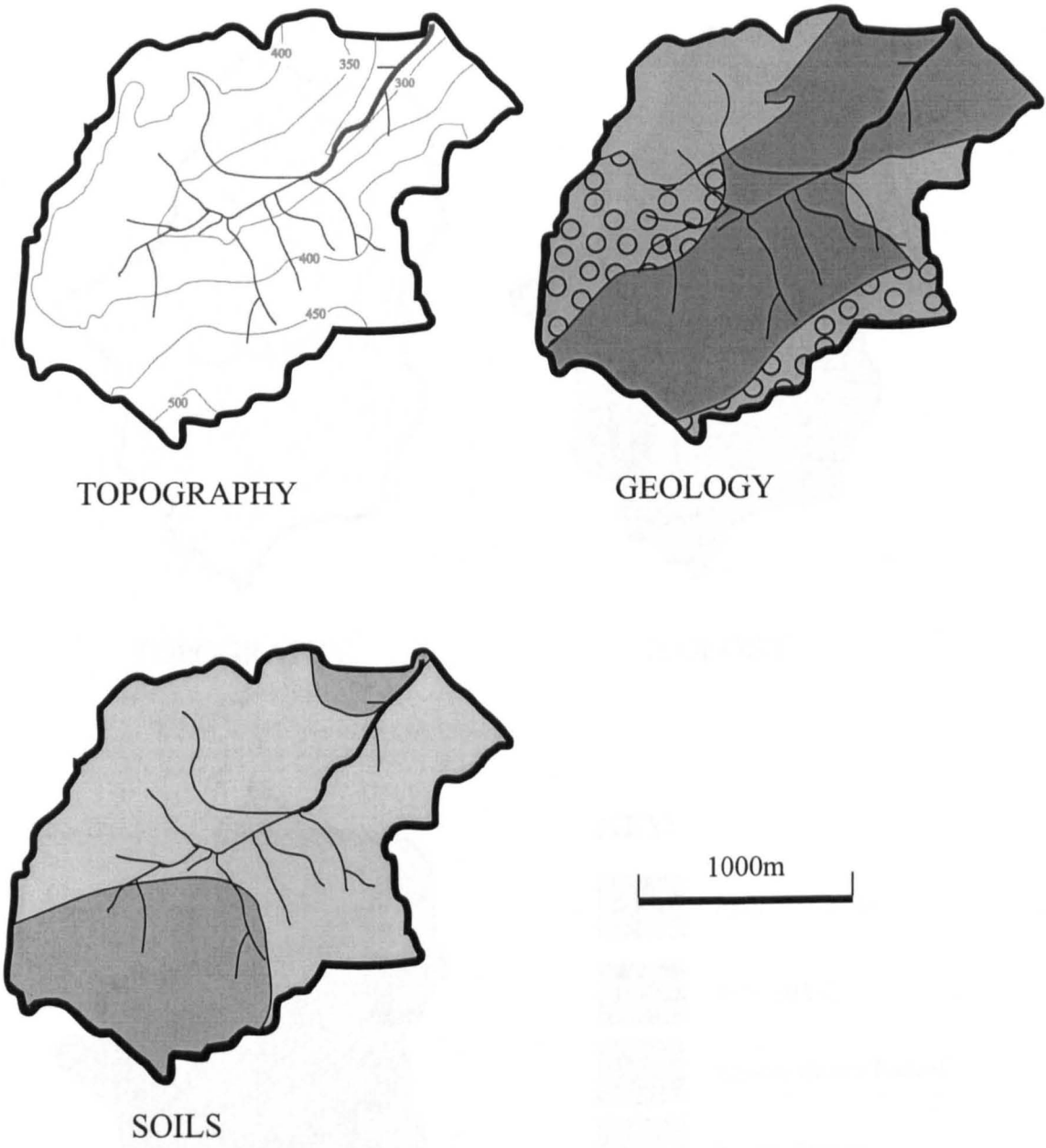


Figure A.56 - Catchment characteristics of Mosedale Beck (Site 54)

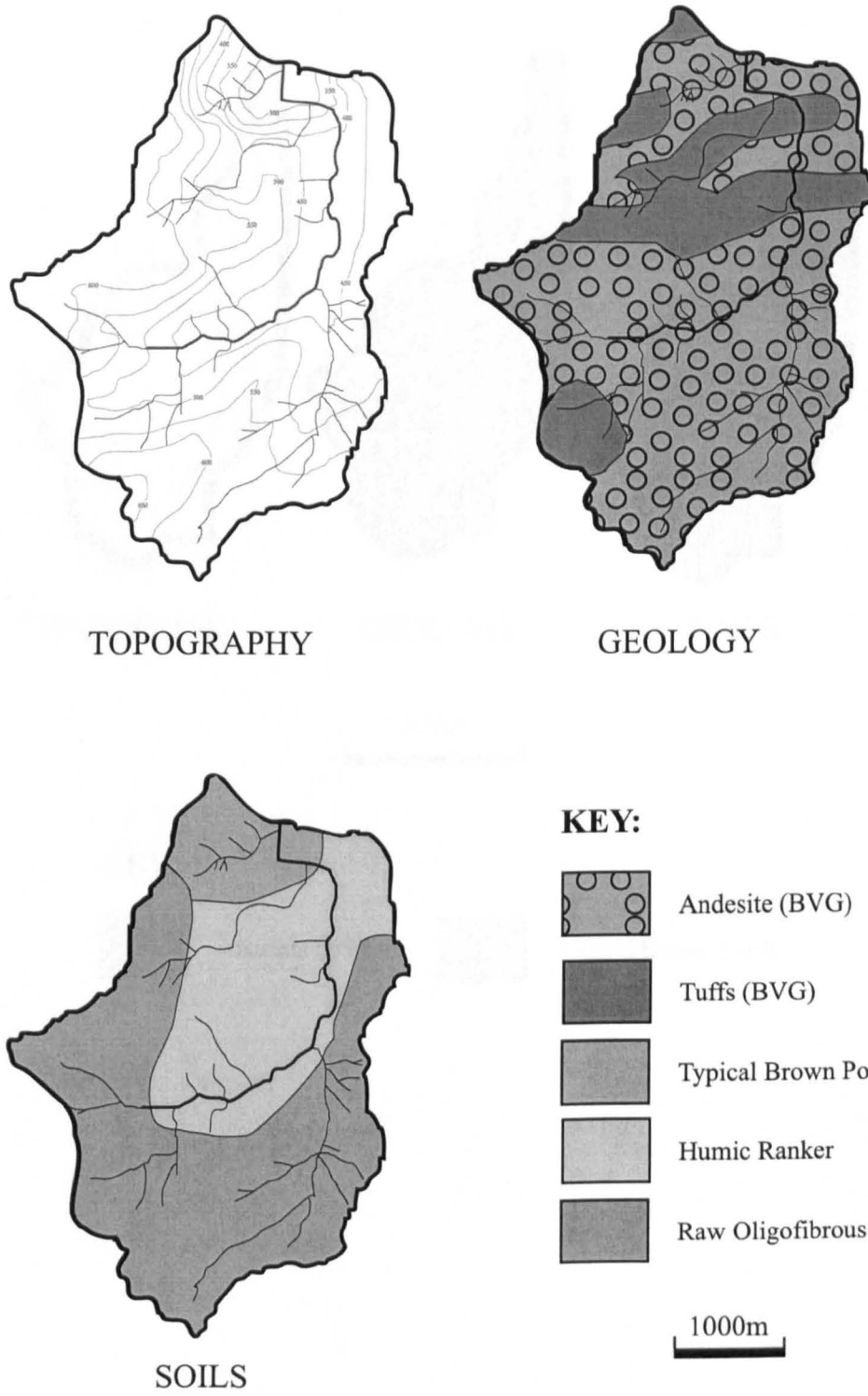
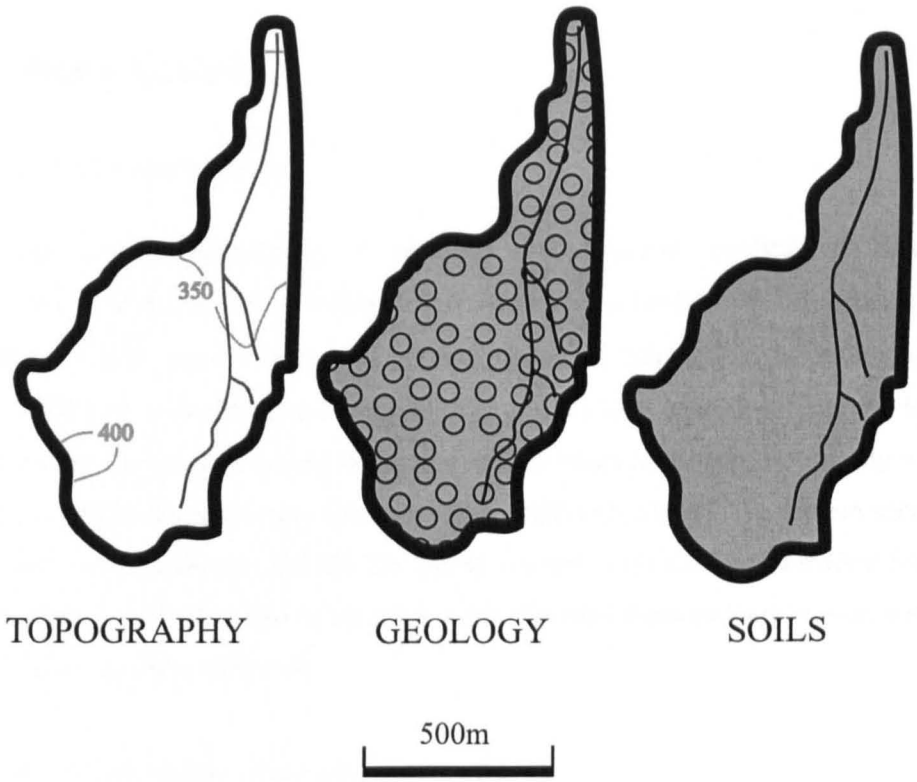


Figure A.57 - Catchment characteristics of Tailbert Gill (Site 55)



APPENDIX B

Analytical Techniques

B.1 Water Analysis

B.1.1 Ion Chromatography

Ion chromatography is a versatile and accurate method of determining concentrations of major ions in solution. This study used a Dionex DX100 system, utilising an IonPac® CG12 guard column and a CS12 analytical column for cation determination, and an IonPac® AG12A guard column and an AS12A analytical column for anion determination. The guard columns increase retention times of the ions but mainly were used to prevent sample contaminants eluting onto the analytical column. The system used for this study comprised the Dionex DX100 ion chromatograph with Self-Regenerating Suppressor control, Dionex AS40 Automated sampler, a Dell General Purpose Data Station and Dionex AI-450 data acquisition software.

B.1.1a Simple principles of ion chromatography

Ion concentrations are determined by measuring conductivity. The conductivity of a solution is measured by applying an alternating voltage between two electrodes in a conductivity cell. Negatively charged anions migrate to the positive electrode and positively charged cations migrate to the negative electrode. The conductivity of a solution is the sum of the individual contributions to conductivity of all the ions in solution multiplied by their concentration (i.e. conductivity is directly proportional to the concentration). The ion chromatograph uses ion exchange to separate the ions into distinct 'peaks'. By using an eluent containing strong electrolytes the DX100 forces ion exchange to occur. However, the concentration of ions in the analyte is overwhelmed by the concentration of ions in the eluent. The DX100 uses chemical suppression to neutralise the eluent in the self-regenerating suppressor. The monovalent ions have shorter retention times than the divalent ions allowing us to characterise each peak as a distinct ion. By measuring the area of each individual peak, we can calculate the concentration in solution relative to a known standard. The DX100 also uses compensation constants to correct for temperature, as temperature drastically effects the mobility of the ions.

B.1.1b Major ion analysis

For cation determination, an eluent of methanesulfonic acid (MSA) was prepared (2.6ml of MSA dissolved into 2 litres of deionised water). For anion determination, an eluent of 2.7mM sodium carbonate (Na_2CO_3) / 0.3mM sodium bicarbonate ($NaHCO_3$) was prepared by dissolving 2.862g of solid Na_2CO_3 and 0.252g of solid $NaHCO_3$ into 100ml deionised water for a concentrate solution and by then dissolving 20ml of concentrate into 2 litres of deionised water for the working stock eluent. The concentrate solution remained fresh for upto 6 months, but the working stock solution was made up prior to every sample run.

The DX100, the automated sampler and the data station were switched on. The eluent container was pressurised to 5-10 pounds per square inch (psi) and the bleed valve was opened to allow any air to escape. The pump was switched on and the flow rate set to 2.0ml per minute and the bleed valve was closed. The flow rate was then reduced to 1.0ml per minute (cations) or 1.25 ml per minute (anions), and the system was allowed to equilibrate for 1 hour. The detector range was set to 30 μS (microsiemens). To establish a baseline the auto offset button was pressed and the background μS allowed to equilibrate.

A method for each determination (cations and anions) was written in the chromatography software, which lists the retention times and concentrations of the 5 standards (Table B1 and Table B2). The retention times may vary due to slight variations in the eluent strength and flow rate.

Table B1 – Retention times and concentrations of Cation Standards 1 to 5
(Run time 11 minutes)

	STD 1	STD 2	STD 3	STD 4	STD 5	Ret. Time
Na^+	2 ppm	5 ppm	10 ppm	15 ppm	20 ppm	3.13 mins
$NH4^+$	0.1 ppm	0.25 ppm	0.5 ppm	0.75 ppm	1 ppm	3.70 mins
K^+	1 ppm	2.5 ppm	5 ppm	7.5 ppm	10 ppm	4.93 mins
Mg^{2+}	1 ppm	2.5 ppm	5 ppm	7.5 ppm	10 ppm	5.67 mins
Ca^{2+}	2 ppm	5 ppm	10 ppm	15 ppm	20 ppm	7.17 mins

Table B.2 – Retention times and concentrations of Anion Standards 1 to 5
(Run time 14 minutes)

	STD 1	STD 2	STD 3	STD 4	STD 5	Ret. Time
F^-	0.1 ppm	0.25 ppm	0.5 ppm	0.75 ppm	1 ppm	2.03 mins
Cl^-	1 ppm	2.5 ppm	5 ppm	7.5 ppm	10 ppm	3.50 mins
NO_3^-	0.5 ppm	1.25 ppm	2.5 ppm	3.75 ppm	5 ppm	8. 33 mins
PO_4^-	0.1 ppm	0.25 ppm	0.5 ppm	0.75 ppm	1 ppm	9.70 mins
SO_4^{2-}	2 ppm	5 ppm	10 ppm	15 ppm	20 ppm	11.90 mins

A schedule for calibrating the system was written in the software with standards labelled AUTOCAL1R through to AUTOCAL5R (Table B3). The automated sampler was loaded with a deionised water sample vial before and after the 5 standards. Once the standards had been analysed the calibration was examined. If the calibration was poor (i.e. if the r^2 of the linear regression through the 5 standards was below 0.99) then the run was aborted and the standards rerun until a satisfactory r^2 was achieved. When a satisfactory r^2 was achieved the samples were analysed. This was repeated for both anions and cations.

Table B3 – Schedule used for calibration of the standards

Inj.	Sample	Method	Datafile	Vol.	Dil.	Int. St.
1	DIW	..\cation.met	..\d01	1	1	1
2	AUTOCAL1R	..\cation.met	..\d02	1	1	1
3	AUTOCAL2R	..\cation.met	..\d03	1	1	1
4	AUTOCAL3R	..\cation.met	..\d04	1	1	1
5	AUTOCAL4R	..\cation.met	..\d05	1	1	1
6	AUTOCAL5R	..\cation.met	..\d06	1	1	1
7	DIW	..\cation.met	..\d07	1	1	1
8	STOP	..\stop.met	..\stop	1	1	1

A schedule was written for the 5 standards and the 55 stream samples, including a deionised water sample, Standards 1 and 5 and another deionised water sample every 10 samples (Table B4). This schedule was repeated for both cations and anions, although only the cation schedule is shown in Table B4.

After each analytical run, the datafiles were examined for misidentified / missed peaks and once checked the datafile was downloaded into Microsoft Excel 5.0 spreadsheets.

Table B4 – Schedule used for each survey period

Inj.	Sample	Method	Datafile	Vol.	Dil.	Int. St.
1	DIW	..\cation.met	..\d01	1	1	1
2	AUTOCAL1R	..\cation.met	..\d02	1	1	1
3	AUTOCAL2R	..\cation.met	..\d03	1	1	1
4	AUTOCAL3R	..\cation.met	..\d04	1	1	1
5	AUTOCAL4R	..\cation.met	..\d05	1	1	1
6	AUTOCAL5R	..\cation.met	..\d06	1	1	1
7	DIW	..\cation.met	..\d07	1	1	1
8	RYDAL BECK	..\cation.met	..\d08	1	1	1
9	STOCK GHYLL	..\cation.met	..\d09	1	1	1
10	HOW BECK	..\cation.met	..\d10	1	1	1
11	DALE PARK BECK	..\cation.met	..\d11	1	1	1
12	LOW CUNSEY B.	..\cation.met	..\d12	1	1	1
13	BELLE GRANGE B	..\cation.met	..\d13	1	1	1
14	RED DELL BECK	..\cation.met	..\d14	1	1	1
15	TORVER BECK	..\cation.met	..\d15	1	1	1
16	WASHFALL BECK	..\cation.met	..\d16	1	1	1
17	MILL BECK 1	..\cation.met	..\d17	1	1	1
18	DIW	..\cation.met	..\d18	1	1	1
19	STD1	..\cation.met	..\d19	1	1	1
20	STD5	..\cation.met	..\d20	1	1	1
21	DIW	..\cation.met	..\d21	1	1	1
22	STONY BECK	..\cation.met	..\d22	1	1	1
↓	↓	↓	↓	↓	↓	↓
95	STD5	..\cation.met	..\d95	1	1	1
96	DIW	..\cation.met	..\d96	1	1	1
97	STOP	..\stop.met	..\stop	1	1	1

B.1.2 pH and Alkalinity

Measurements of pH and Gran alkalinity were carried out under laboratory conditions at the Open University. A Mettler Toledo pH electrode with auto-temperature calibration (ATC) was used for the pH and alkalinity determinations. Samples were kept airtight and refrigerated below 4°C in 50 ml glass bottles. Samples were usually analysed within two weeks to minimise any chemical alteration.

B.1.2a pH determination

The pH electrode was calibrated using pH 4.0 and pH 7.0 buffers prior to analysis and the accuracy was checked by measuring the pH of the buffer solutions every 10 samples during analysis. Water samples were poured into a clean 100ml Pyrex® beaker and the pH electrode was immersed in the sample. The pH was recorded immediately after stirring and at the quiescent stage (i.e. after no change in the pH reading for 30 seconds).

B.1.2b Alkalinity determination

To calculate alkalinity the mass of the water sample is required. Since the mass of water analysed was always the mass of water in a full 50ml glass bottle, this amount was estimated by measuring eight different 50ml glass sample bottles empty and then full (Table B5). The average volume was then used in the subsequent calculation of alkalinity.

Table B5 – Measuring the mass of water in eight glass bottles

Bottle	Empty bottle	Brimful Bottle	Sample volume
1	67.169 g	122.841 g	55.672 g
2	67.232 g	123.511g	56.279 g
3	67.067 g	123.584 g	56.517 g
4	67.375 g	122.967 g	55.592 g
5	67.279 g	123.610 g	56.331 g
6	67.247 g	123.185 g	55.938 g
7	66.977 g	123.058 g	56.081 g
8	67.087 g	123.133 g	56.046 g
Min			**55.592 g**
Max			**56.517 g**
Mean			**56.057 g**

The alkalinity determination was carried out whilst the sample from the pH determination was in the beaker. Alkalinity was determined using the reference method of

Gran (1952). The titrant prepared for the Gran titration was a 0.01 N sulphuric acid (H_2SO_4) solution. To achieve the working solution, 10 ml of 0.5 N sulphuric acid was diluted into 500 ml of deionised water. The titrant was added to the sample in 0.1ml intervals and mixed with a magnetic stirrer until a pH of 4.5 or less was reached. The exact pH and the number of ml titrated were recorded. The titrant was then added to the sample in 0.1ml intervals until a pH of 4.0 or less was reached. Again the exact pH and number of ml titrated were recorded. The titrant was then added in 1.0ml intervals until a pH of 3.0 or less was reached. Again the exact pH and number of ml titrated was recorded. This data was entered into a Microsoft Excel 5.0 spreadsheet to calculate Gran Alkalinity (C. Neal, personal communication). The spreadsheet contained several complex formulae (Appendix C) but written simply, Gran alkalinity is represented by the following equation:

$$\mathbf{Alk_{Gran} = HCO_3^- - H^+ + 4Al(OH)_4^- + 3Al(OH)_3^0 + 2Al(OH)_2^+ + Al(OH)^{2+} + Alk_{org}}$$

Where **Alk_{Gran}** is Gran alkalinity
Alk_{org} is the contribution by organics (pH 4 to 3)

B.1.3 Silica analysis

The dissolved silica content of the streamwater was determined under laboratory conditions at The Open University. The concentrations of silica present were determined photometrically by molybdate reactive analysis using an adaptation of the reference method of Webber & Wilson (1964), which requires three analytical grade reagents.

(1) Molybdate solution – 63 ml sulphuric acid was dissolved into 100 ml deionised water and allowed to cool and 89g ammonium molydate (NH_4 6M O_7O_{24} $4H_2O$) was dissolved into 800 ml deionised water. The sulphuric acid solution and the molydate solution were then added together and made up to 1 litre with deionised water.

(2) Tartaric acid solution – 70g tartaric acid was dissolved into 250 ml deionised water.

(3) ANSA solution – 1.2g sodium sulphite anhydrous (Na_2SO_3) and 0.2g 1-amino-2-naphtol-4-sulphonic acid were dissolved into 70 ml deionised water. Then 14g potassium metabisulphite ($K_2S_2O_5$) was dissolved into the solution and diluted to 100 ml with deionised water.

Five millilitres of each stream sample was diluted (to approximately 40 ml) with deionised water in 50ml volumetric flasks. Exactly 1.25 ml of molydate solution was added and mixed immediately. After ten minutes, exactly 1.25 ml of the tartaric acid solution was added and mixed immediately. After a further 5 minutes, exactly 1.0 ml of the ANSA solution was added and mixed thoroughly. The sample was diluted upto the 50 ml line with deionised water. The solutions were transferred into 1 cm cuvettes between 20 and 60 minutes later and the optical densities were measured using a Photospectrometer at 820 nm.

B.2 Whole rock (XRF) analysis

B.2.1 Major Element analysis

Major element analyses were made on an ARL 8420+ dual goniometer wavelength dispersive XRF spectrometer, equipped with 3 kW Rh anode end-window X-ray tube, flow proportional and scintillation counters (fully collimated), and diffracting crystals (AX06 – multi-layer; PET – pentaerythrytol; Ge111; LiF200; LiF220). The operating conditions during analysis are described in Webb & Watson (1996). The glass discs are also archived at The Open University.

B.2.2 Trace Element analysis

Trace element analyses were made with the same ARL 8420+ XRF spectrometer used for major element analyses. The operating conditions during analysis are described in Webb & Watson (1996). The powder pellets are also archived at The Open University.

APPENDIX C

Standards

C.1 Major-ion standards

The range in water concentrations of each chemical constituent in typical upland streams was found by examining several published papers. The upper and lower limits of the analytical standards chosen for the ion chromatography work were based upon the data found in this literature search. Internal anion and cation standards were made up on the day of the sample run, and standards from the Institute of Hydrology, UK were incorporated for inter-laboratory quality control. The concentrations of the standards used in this study can be found in Table C1.

Table C1 – Cation and Anion standards used in this study
(Units are mg/l)

	STD 1	STD 2	STD 3	STD 4	STD 5	IHSTD 1	IHSTD 2
Na^+	2.00	5.00	10.00	15.00	20.00	0.20	2.00
$NH4^+$	0.10	0.25	0.50	0.75	1.00	0.20	2.00
K^+	1.00	2.50	5.00	7.50	10.00	0.20	2.00
Mg^{2+}	1.00	2.50	5.00	7.50	10.00	0.20	2.00
Ca^{2+}	2.00	5.00	10.00	15.00	20.00	0.40	4.00
F^-	0.10	0.25	0.50	0.75	1.00	0.10	0.50
Cl^-	1.00	2.50	5.00	7.50	10.00	2.00	10.00
NO_3^-	0.50	1.25	2.50	3.75	5.00	0.20	1.00
PO_4^-	0.10	0.25	0.50	0.75	1.00	0.40	2.00
SO_4^{2-}	2.00	5.00	10.00	15.00	20.00	2.00	10.00

All five internal standards were analysed at the beginning and end of each sample run, and the highest and lowest standards were analysed every 10 samples to examine whether any 'drift' occurred during the analyses. In addition, the Institute of Hydrology standards were analysed on the first, third and fifth trip to allow inter-laboratory control. The analytical data was 'lifted' from each data run and are presented in sequence (Tables C2 to C13). All of the recorded data for the standards are within ± 5% of the 'original' standards in Table C1.

Table C2 – Ion chromatograph data for the cation standards in May 1996

(Units are in mg/l)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
CALPLOT (r-sq)	0.999	0.994	0.997	1.002	0.997
CATION STD1	1.998	0.105	0.998	0.996	1.997
CATION STD2	4.996	0.248	2.486	2.453	5.052
CATION STD3	10.120	0.487	4.967	4.997	10.057
CATION STD4	14.976	0.749	7.487	7.497	14.996
CATION STD5	19.986	0.997	9.958	9.998	19.955
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.227	0.204	0.197	0.210	0.418
IH STD 2	2.155	1.995	2.031	2.034	4.098
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1 (10)	2.125	0.086	0.988	0.982	1.943
CATION STD5 (10)	19.753	0.988	9.832	9.885	19.883
CATION STD1 (20)	2.080	0.099	0.980	0.985	1.979
CATION STD5 (20)	19.829	0.992	9.945	9.970	20.069
CATION STD1 (30)	2.095	0.097	1.052	0.976	1.990
CATION STD5 (30)	19.884	0.993	9.981	10.023	20.061
CATION STD1 (40)	2.121	0.099	0.987	1.010	1.962
CATION STD5 (40)	19.824	0.980	9.957	10.127	20.255
CATION STD1 (50)	2.038	0.104	0.988	0.985	1.998
CATION STD5 (50)	20.248	1.057	10.217	10.304	20.138
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1	2.118	0.099	0.993	0.977	1.988
CATION STD2	5.216	0.249	2.531	2.526	5.045
CATION STD3	10.351	0.495	5.047	5.101	10.071
CATION STD4	15.311	0.769	7.514	7.535	15.439
CATION STD5	19.634	1.045	9.982	10.259	20.031
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.211	0.202	0.199	0.213	0.404
IH STD 2	2.094	2.041	2.057	2.059	4.027

Table C3 – Ion chromatograph data for the anion standards in May 1996

(Units are in mg/l)

	F^-	Cl^-	NO_3^-	PO_4^-	SO_4^{2-}
CALPLOT (r-sq)	0.998	1.027	1.005	1.005	1.005
ANION STD1	0.096	0.941	0.471	0.098	1.962
ANION STD2	0.249	2.450	1.231	0.254	4.904
ANION STD3	0.495	4.855	2.454	0.498	9.913
ANION STD4	0.745	7.549	3.725	0.745	15.019
ANION STD5	0.997	10.188	5.000	1.008	20.009
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.113	2.092	0.235	0.399	2.016
IH STD 2	0.489	10.108	1.130	2.007	10.132
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1 (10)	0.101	0.968	0.506	0.095	1.958
ANION STD5 (10)	1.013	10.151	5.006	1.002	20.052
ANION STD1 (20)	0.099	0.988	0.513	0.097	1.979
ANION STD5 (20)	1.022	10.082	5.051	1.003	20.160
ANION STD1 (30)	0.096	0.993	0.505	0.097	1.950
ANION STD5 (30)	1.012	10.040	4.984	0.098	20.127
ANION STD1 (40)	0.098	0.969	0.483	0.094	1.943
ANION STD5 (40)	1.034	10.040	4.978	1.001	20.163
ANION STD1 (50)	0.096	0.985	0.481	0.104	1.981
ANION STD5 (50)	1.028	10.134	5.082	1.003	20.118
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1	0.099	0.988	0.506	0.102	1.968
ANION STD2	0.254	2.486	1.268	0.248	5.080
ANION STD3	0.501	4.962	2.502	0.510	10.009
ANION STD4	0.773	7.519	3.769	0.745	15.146
ANION STD5	1.001	10.028	5.062	1.009	20.042
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.109	2.062	0.230	0.390	2.015
IH STD 2	0.503	10.091	1.133	2.083	10.183

Table C4 – Ion chromatograph data for the cation standards in July 1996

(Units are in mg/l)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
CALPLOT (r-sq)	0.999	0.994	0.997	0.996	1.002
CATION STD1	1.998	0.105	0.998	0.996	1.997
CATION STD2	4.996	0.248	2.486	2.453	5.052
CATION STD3	10.120	0.487	4.967	4.997	10.057
CATION STD4	14.976	0.749	7.487	7.497	14.996
CATION STD5	19.986	0.997	9.958	9.998	19.955
DIW	0.000	0.000	0.000	0.000	0.000
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1 (10)	1.998	0.100	0.999	0.995	2.056
CATION STD5 (10)	19.996	1.008	10.075	10.064	20.073
CATION STD1 (20)	2.075	0.103	1.046	1.043	1.996
CATION STD5 (20)	19.962	0.998	9.996	9.998	19.996
CATION STD1 (30)	2.080	0.099	0.980	0.985	1.979
CATION STD5 (30)	19.829	0.992	9.945	9.970	20.069
CATION STD1 (40)	2.095	0.097	1.052	0.976	1.990
CATION STD5 (40)	19.884	0.993	9.981	10.023	20.061
CATION STD1 (50)	2.121	0.099	0.987	1.010	1.962
CATION STD5 (50)	19.824	0.980	9.957	10.127	20.255
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1	1.997	0.097	0.999	0.993	1.996
CATION STD2	4.993	0.250	2.495	2.496	4.997
CATION STD3	10.047	0.496	5.027	5.062	10.056
CATION STD4	15.027	0.751	7.496	7.515	15.058
CATION STD5	20.045	1.004	10.025	9.999	19.999
DIW	0.000	0.000	0.000	0.000	0.000

Table C5 – Ion chromatograph data for the anion standards in July 1996

(Units are in mg/l)

	F^-	Cl^-	NO_3^-	PO_4^-	SO_4^{2-}
CALPLOT (r-sq)	0.995	1.003	1.000	0.988	0.984
ANION STD1	0.099	0.997	0.498	0.100	1.997
ANION STD2	0.249	2.494	1.260	0.249	4.450
ANION STD3	0.495	4.919	2.502	0.489	9.485
ANION STD4	0.748	7.482	3.761	0.748	14.361
ANION STD5	0.994	10.012	4.998	0.987	19.627
DIW	0.000	0.000	0.000	0.000	0.000
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1 (10)	0.100	0.985	0.481	0.099	1.993
ANION STD5 (10)	1.000	10.027	4.973	0.990	20.104
ANION STD1 (20)	0.098	0.985	0.492	0.099	1.982
ANION STD5 (20)	0.993	10.096	4.995	0.987	20.041
ANION STD1 (30)	0.099	0.994	0.497	0.100	1.983
ANION STD5 (30)	1.013	10.126	4.985	0.984	20.027
ANION STD1 (40)	0.099	0.988	0.497	0.098	1.980
ANION STD5 (40)	0.996	10.126	4.984	0.993	20.120
ANION STD1 (50)	0.099	0.999	0.494	0.099	1.987
ANION STD5 (50)	0.989	10.092	4.976	0.988	20.041
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1	0.099	0.991	0.463	0.099	1.988
ANION STD2	0.253	2.486	1.249	0.249	4.996
ANION STD3	0.475	4.973	2.485	0.487	9.984
ANION STD4	0.747	7.465	3.736	0.760	14.975
ANION STD5	0.994	10.090	4.980	0.979	20.010
DIW	0.000	0.000	0.000	0.000	0.000

Table C6 – Ion chromatograph data for the cation standards in Sept 1996

(Units are in mg/l)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
CALPLOT (r-sq)	1.003	1.007	1.002	1.001	1.001
CATION STD1	1.997	0.097	0.999	0.993	1.996
CATION STD2	4.993	0.250	2.495	2.496	4.997
CATION STD3	10.047	0.496	5.027	5.062	10.056
CATION STD4	15.027	0.751	7.496	7.515	15.058
CATION STD5	20.045	1.004	10.025	9.999	19.999
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.201	0.200	0.201	0.200	0.398
IH STD 2	2.018	1.987	1.992	2.018	4.028
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1 (10)	1.998	0.100	0.999	0.995	2.056
CATION STD5 (10)	19.996	1.008	10.075	10.064	20.073
CATION STD1 (20)	2.075	0.103	1.046	1.043	1.996
CATION STD5 (20)	19.962	0.998	9.996	9.998	19.996
CATION STD1 (30)	1.996	0.100	1.003	1.002	1.996
CATION STD5 (30)	19.986	1.067	10.067	10.057	19.994
CATION STD1 (40)	1.999	0.106	1.082	1.056	2.005
CATION STD5 (40)	20.057	1.029	10.024	10.028	20.043
CATION STD1 (50)	2.066	0.099	0.999	0.999	1.998
CATION STD5 (50)	19.994	0.993	10.098	9.986	19.997
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1	1.992	0.106	0.998	1.057	2.054
CATION STD2	4.997	0.250	2.498	2.504	4.986
CATION STD3	10.072	0.504	4.967	5.025	10.036
CATION STD4	15.025	0.749	7.493	7.526	14.997
CATION STD5	19.995	1.057	10.052	10.085	19.995
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.201	0.199	0.201	0.202	0.391
IH STD 2	2.104	1.981	2.017	1.994	4.017

Table C7 – Ion chromatograph data for the anion standards in Sept 1996

(Units are in mg/l)

	F^-	Cl^-	NO_3^-	PO_4^-	SO_4^{2-}
CALPLOT (r-sq)	1.031	1.000	0.999	1.052	0.999
ANION STD1	0.105	0.997	0.500	0.100	1.998
ANION STD2	0.250	2.495	1.250	0.250	4.994
ANION STD3	0.500	5.027	2.497	0.496	10.057
ANION STD4	0.749	7.493	3.746	0.749	14.967
ANION STD5	1.038	9.994	4.993	1.058	19.996
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.103	2.093	0.234	0.399	2.016
IH STD 2	0.499	10.097	1.129	2.002	10.013
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1 (10)	0.101	1.082	0.500	0.100	1.996
ANION STD5 (10)	1.059	10.024	5.057	1.008	20.057
ANION STD1 (20)	0.100	0.999	0.504	0.103	1.998
ANION STD5 (20)	1.068	10.098	5.026	0.998	19.996
ANION STD1 (30)	0.099	0.995	0.500	0.100	2.075
ANION STD5 (30)	0.995	10.064	4.996	1.067	19.993
ANION STD1 (40)	0.106	1.043	0.504	0.101	1.997
ANION STD5 (40)	1.057	9.998	5.027	1.059	19.997
ANION STD1 (50)	0.099	1.002	0.500	0.100	1.996
ANION STD5 (50)	0.993	10.057	4.996	1.068	20.047
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1	0.101	1.007	0.499	0.097	2.052
ANION STD2	0.250	2.496	1.249	0.250	4.996
ANION STD3	0.494	5.007	2.490	0.496	10.057
ANION STD4	0.748	7.494	3.749	0.751	15.035
ANION STD5	1.076	10.067	5.002	1.004	20.048
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.108	2.061	0.231	0.400	2.013
IH STD 2	0.502	10.097	1.134	2.087	10.071

Table C8 – Ion chromatograph data for the cation standards in Nov 1996

(Units are in mg/l)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
CALPLOT (r-sq)	1.001	1.003	0.997	1.004	1.001
CATION STD1	1.998	0.100	1.025	1.004	1.994
CATION STD2	4.991	0.250	2.498	2.503	5.014
CATION STD3	10.014	0.502	4.994	4.997	10.052
CATION STD4	15.047	0.748	7.491	7.495	14.996
CATION STD5	19.997	1.003	9.997	10.053	20.027
DIW	0.000	0.000	0.000	0.000	0.000
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1 (10)	2.125	0.086	0.988	0.982	1.943
CATION STD5 (10)	19.753	0.988	9.832	9.885	19.883
CATION STD1 (20)	2.080	0.099	0.980	0.985	1.979
CATION STD5 (20)	19.829	0.992	9.945	9.970	20.069
CATION STD1 (30)	2.095	0.097	1.052	0.976	1.990
CATION STD5 (30)	19.884	0.993	9.981	10.023	20.061
CATION STD1 (40)	2.121	0.099	0.987	1.010	1.962
CATION STD5 (40)	19.824	0.980	9.957	10.127	20.255
CATION STD1 (50)	2.038	0.104	0.988	0.985	1.998
CATION STD5 (50)	20.248	1.057	10.217	10.304	20.138
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1	1.992	0.106	0.998	1.057	2.054
CATION STD2	4.997	0.250	2.498	2.504	4.986
CATION STD3	10.072	0.504	4.967	5.025	10.036
CATION STD4	15.025	0.749	7.493	7.526	14.997
CATION STD5	19.995	1.057	10.052	10.085	19.995
DIW	0.000	0.000	0.000	0.000	0.000

Table C9 – Ion chromatograph data for the anion standards in Nov 1996

(Units are in mg/l)

	F^-	Cl^-	NO_3^-	PO_4^-	SO_4^{2-}
CALPLOT (r-sq)	0.995	1.003	1.000	0.988	0.984
ANION STD1	0.099	0.997	0.498	0.100	1.997
ANION STD2	0.249	2.494	1.260	0.249	4.450
ANION STD3	0.495	4.820	2.502	0.489	9.485
ANION STD4	0.748	7.482	3.761	0.748	14.361
ANION STD5	0.994	10.012	4.998	0.987	19.627
DIW	0.000	0.000	0.000	0.000	0.000
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1 (10)	0.101	0.968	0.500	0.100	1.996
ANION STD5 (10)	1.013	10.151	5.057	1.008	20.057
ANION STD1 (20)	0.099	0.988	0.504	0.103	1.998
ANION STD5 (20)	1.022	10.082	5.026	0.998	19.996
ANION STD1 (30)	0.096	0.993	0.500	0.100	2.075
ANION STD5 (30)	1.012	10.040	4.996	1.067	19.993
ANION STD1 (40)	0.098	0.969	0.504	0.101	1.997
ANION STD5 (40)	1.034	10.040	5.027	1.059	19.997
ANION STD1 (50)	0.096	0.985	0.500	0.100	1.996
ANION STD5 (50)	1.028	10.134	4.996	1.068	20.047
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1	0.099	1.007	0.499	0.099	1.988
ANION STD2	0.254	2.496	1.249	0.249	4.996
ANION STD3	0.501	5.007	2.490	0.487	9.984
ANION STD4	0.773	7.494	3.749	0.760	14.975
ANION STD5	1.001	10.067	5.002	0.979	20.010
DIW	0.000	0.000	0.000	0.000	0.000

Table C10 – Ion chromatograph data for the cation standards in Jan 1997

(Units are in mg/l)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
CALPLOT (r-sq)	0.997	1.050	1.002	1.001	1.010
CATION STD1	1.997	0.099	0.999	0.993	1.988
CATION STD2	5.052	0.249	2.495	2.496	5.045
CATION STD3	10.057	0.495	5.027	5.062	10.071
CATION STD4	14.996	0.769	7.496	7.515	15.439
CATION STD5	19.955	1.045	10.025	9.999	20.031
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.202	0.200	0.199	0.202	0.400
IH STD 2	2.014	1.997	1.985	2.013	3.994
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1 (10)	1.993	0.973	1.001	0.985	1.958
CATION STD5 (10)	19.996	1.039	10.026	10.027	20.052
CATION STD1 (20)	2.071	0.981	0.995	0.985	1.979
CATION STD5 (20)	19.984	1.014	10.032	10.096	20.160
CATION STD1 (30)	1.998	0.102	1.024	0.994	1.950
CATION STD5 (30)	20.014	1.035	9.996	10.126	20.127
CATION STD1 (40)	1.996	0.999	0.998	0.988	1.943
CATION STD5 (40)	19.994	1.012	9.997	10.126	20.163
CATION STD1 (50)	2.013	0.105	1.021	0.999	1.981
CATION STD5 (50)	20.017	1.052	10.014	10.092	20.118
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1	1.998	0.105	0.993	0.977	1.997
CATION STD2	4.996	0.248	2.531	2.526	5.052
CATION STD3	10.120	0.487	5.047	5.101	10.057
CATION STD4	14.976	0.749	7.514	7.535	14.996
CATION STD5	19.986	0.997	9.982	10.259	19.955
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.210	0.201	0.199	0.200	0.398
IH STD 2	2.041	1.995	1.995	2.034	4.015

Table C11 – Ion chromatograph data for the anion standards in Jan 1997

(Units are in mg/l)

	F^-	Cl^-	NO_3^-	PO_4^-	SO_4^{2-}
CALPLOT (r-sq)	0.994	1.008	1.001	0.988	0.984
ANION STD1	0.099	0.991	0.463	0.100	1.997
ANION STD2	0.253	2.486	1.249	0.249	4.450
ANION STD3	0.475	4.973	2.485	0.489	9.485
ANION STD4	0.747	7.465	3.736	0.748	14.361
ANION STD5	0.994	10.090	4.980	0.987	19.627
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.104	2.091	0.233	0.397	2.013
IH STD 2	0.500	10.054	1.135	1.994	10.041
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1 (10)	0.100	0.982	0.500	0.101	2.056
ANION STD5 (10)	1.008	9.885	5.012	1.013	20.073
ANION STD1 (20)	0.103	0.985	0.504	0.099	1.996
ANION STD5 (20)	0.998	9.970	4.992	1.022	19.996
ANION STD1 (30)	0.100	0.976	0.493	0.096	1.979
ANION STD5 (30)	1.067	10.023	5.053	1.012	20.069
ANION STD1 (40)	0.101	1.010	0.501	0.098	1.990
ANION STD5 (40)	1.059	10.127	4.992	1.034	20.061
ANION STD1 (50)	0.100	0.985	0.492	0.096	1.962
ANION STD5 (50)	1.068	10.304	4.993	1.028	20.255
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1	0.099	0.941	0.471	0.099	1.988
ANION STD2	0.249	2.450	1.231	0.249	4.996
ANION STD3	0.495	4.855	2.454	0.487	9.984
ANION STD4	0.748	7.549	3.725	0.760	14.975
ANION STD5	0.994	10.188	5.000	0.979	20.010
DIW	0.000	0.000	0.000	0.000	0.000
IH STD 1	0.099	2.031	0.232	0.405	1.997
IH STD 2	0.501	9.995	1.136	2.065	9.994

Table C12 – Ion chromatograph data for the cation standards in Mar 1997

(Units are in mg/l)

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
CALPLOT (r-sq)	0.994	0.996	0.994	0.994	0.995
CATION STD1	1.997	0.097	0.999	0.993	1.996
CATION STD2	4.993	0.250	2.495	2.496	4.997
CATION STD3	10.047	0.496	5.027	5.062	10.056
CATION STD4	15.027	0.751	7.496	7.515	15.058
CATION STD5	20.045	1.004	10.025	9.999	19.999
DIW	0.000	0.000	0.000	0.000	0.000
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1 (10)	2.075	0.103	1.046	1.043	1.996
CATION STD5 (10)	19.962	0.998	9.996	9.998	19.996
CATION STD1 (20)	2.071	0.981	0.995	0.985	1.979
CATION STD5 (20)	19.984	1.014	10.032	10.096	20.160
CATION STD1 (30)	1.997	0.099	0.999	0.993	1.988
CATION STD5 (30)	19.955	1.045	10.025	9.999	20.031
CATION STD1 (40)	1.998	0.105	0.993	0.977	1.997
CATION STD5 (40)	19.986	0.997	9.882	10.259	19.955
CATION STD1 (50)	2.095	0.097	1.052	0.976	1.990
CATION STD5 (50)	19.884	0.993	9.981	10.023	20.061
DIW	0.000	0.000	0.000	0.000	0.000
CATION STD1	2.118	0.099	0.993	0.977	1.988
CATION STD2	5.216	0.249	2.531	2.526	5.045
CATION STD3	10.351	0.495	5.047	5.101	10.071
CATION STD4	15.311	0.769	7.514	7.535	15.439
CATION STD5	19.634	1.045	9.982	10.259	20.031
DIW	0.000	0.000	0.000	0.000	0.000

Table C13 – Ion chromatograph data for the anion standards in Mar 1997

(Units are in mg/l)

	F^-	Cl^-	NO_3^-	PO_4^-	SO_4^{2-}
CALPLOT (r-sq)	0.996	0.986	0.997	0.995	0.999
ANION STD1	0.099	0.997	0.498	0.100	1.997
ANION STD2	0.249	2.494	1.260	0.249	4.450
ANION STD3	0.495	4.920	2.502	0.489	9.485
ANION STD4	0.748	7.482	3.761	0.748	14.361
ANION STD5	0.994	10.012	4.998	0.987	19.627
DIW	0.000	0.000	0.000	0.000	0.000
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1 (10)	0.098	0.985	0.492	0.099	1.982
ANION STD5 (10)	0.993	10.096	4.995	0.987	20.041
ANION STD1 (20)	0.103	0.985	0.504	0.099	1.996
ANION STD5 (20)	0.998	9.970	4.992	1.022	19.996
ANION STD1 (30)	0.099	0.991	0.463	0.100	1.997
ANION STD5 (30)	0.994	10.090	4.980	0.987	19.627
ANION STD1 (40)	0.099	0.941	0.471	0.099	1.988
ANION STD5 (40)	0.994	10.188	5.000	0.979	20.010
ANION STD1 (50)	0.096	0.993	0.505	0.097	1.950
ANION STD5 (50)	1.012	10.040	4.984	0.098	20.127
DIW	0.000	0.000	0.000	0.000	0.000
ANION STD1	0.099	0.988	0.506	0.102	1.968
ANION STD2	0.254	2.486	1.268	0.248	5.080
ANION STD3	0.501	4.962	2.502	0.510	10.009
ANION STD4	0.773	7.519	3.769	0.745	15.146
ANION STD5	1.001	10.028	5.062	1.009	20.042
DIW	0.000	0.000	0.000	0.000	0.000

C.2 pH standards

Two pH buffer solutions were used, pH 4 and pH 7. The pH electrode was calibrated with both buffers prior to each sample run and every 10 samples to examine whether any 'drift' occurred during the analyses. The measured buffer pH always ranged between 4.00-4.02 and 7.00-7.02 throughout the sample runs.

C.3 Gran alkalinity titration data

Tables C14 to C18 give the Gran alkalinity titration data for the surveys. The column headings in Tables C14 to C18 represent the following formulae:

[1] $$Alk_{Gran1} = \left[V_1 - \left[\frac{V_0 + V_1 * 10^{-pH4.5}}{Ct_1} \right] * 10^6 \right] * \frac{\overline{C}_A}{V_0}$$

[2] $$Alk_{Gran2} = \left[V_2 - \left[\frac{V_0 + V_2 * 10^{-pH4}}{Ct_2} \right] * 10^6 \right] * \frac{\overline{C}_A}{V_0}$$

[3] $$Ct_1 = \left[\frac{(V_0 + V_2 * 10^{-pH4}) - (V_0 + V_1 * 10^{-pH4.5})}{V_2 - V_1} \right]$$

[4] $$Ct_2 = \left[\frac{(V_0 + V_3 * 10^{-pH3}) - (V_0 + V_2 * 10^{-pH4})}{V_3 - V_2} \right]$$

[5] $$E.pCO_2 = \frac{[H^+]\,[HCO_3^-]}{5.25}$$

Where

Alk_{Gran1} is Gran alkalinity in the pH range 4.5 – 4.0 (μeq/l)
Alk_{Gran2} is Gran alkalinity in the pH range 4.0 – 3.0 (μeq/l)
V_0 is the original volume of the sample (ml)
V_1 is the volume of titrant added to pH 4.5 (ml)
V_2 is the volume of titrant added to pH 4.0 (ml)
V_3 is the volume of titrant added to pH 3.0 (ml)
Ct_1 is the calculated titrant strength 1 (see equation 3)
Ct_2 is the calculated titrant strength 2 (see equation 4)
C_A is the acid strength in Eq/l
pCO_2 is the partial pressure of degassing carbon dioxide

Table C14 – Gran alkalinity titration data in July 1996

Sample	pH	V_0	C_A	V_1	pH ~ 4.5	V_2	pH ~ 4.0	V_3	pH ~ 3.0	Alk_{Gran1}	Ct_1	Alk_{Gran2}	Ct_2	pCO_2
1	6.99	56.05	0.01	0.5	4.31	0.6	3.93	3.6	2.95	76.49	0.039	47.94	0.020	1.49
2	7.81	56.05	0.01	0.8	4.34	1	3.77	3	3	129.65	0.035	108.38	0.025	0.38
3	7.36	56.05	0.01	1.2	4.19	1.3	3.88	4.3	2.97	197.03	0.039	161.08	0.019	1.64
4	7	56.05	0.01	0.7	4.33	0.8	3.97	3.8	2.96	111.11	0.034	87.96	0.020	2.12
5	7.92	56.05	0.01	1.6	4.12	1.7	3.83	4.7	2.85	266.74	0.042	244.13	0.026	0.61
6	7.48	56.05	0.01	0.8	4.28	0.9	3.94	3.9	2.92	127.76	0.036	107.17	0.022	0.81
7	7.01	56.05	0.01	0.3	4.25	0.4	3.92	3.4	2.96	37.90	0.036	9.16	0.019	0.71
8	7.38	56.05	0.01	0.6	4.17	0.7	3.87	3.7	2.94	89.18	0.038	57.66	0.020	0.71
9	7.49	56.05	0.01	1.3	4.28	1.4	3.93	4.4	2.91	217.58	0.037	196.35	0.023	1.34
10	8.06	56.05	0.01	2.3	4.5	2.5	3.83	5.5	2.87	400.69	0.034	383.70	0.025	0.66
11	7.45	56.05	0.01	0.7	4.22	0.8	3.87	3.8	2.89	110.53	0.042	83.61	0.023	0.75
12	7.81	56.05	0.01	0.8	4.36	0.9	3.94	3.9	2.83	131.82	0.041	117.96	0.027	0.39
13	7.49	56.05	0.01	0.8	4.21	0.9	3.83	2.9	3	130.01	0.049	101.08	0.025	0.80
14	7.85	56.05	0.01	0.9	4.22	1	3.86	4	2.86	146.79	0.044	122.22	0.025	0.39
15	8.24	56.05	0.01	3.8	4.29	4.1	3.82	7.1	2.9	650.74	0.020	662.27	0.023	0.71
16	8.22	56.05	0.01	2.5	4.47	2.7	3.79	5.7	2.88	436.65	0.038	410.76	0.024	0.50
17	7.98	56.05	0.01	3.3	4.21	3.4	3.86	6.4	2.86	574.40	0.045	550.29	0.026	1.15
20	7.86	56.05	0.01	3.9	4.29	4	3.91	7	2.92	683.09	0.043	655.85	0.023	1.80
21	7.18	56.05	0.01	1.2	4.21	1.3	3.91	4.3	3	196.23	0.035	161.08	0.018	2.47
22	7.87	56.05	0.01	1.6	4.41	1.7	3.95	4.7	2.97	276.01	0.042	244.13	0.020	0.71
23	7.69	56.05	0.01	1.2	4.23	1.3	3.93	4.3	2.98	196.23	0.034	168.06	0.019	0.76
24	7.79	56.05	0.01	2.2	4.14	2.3	3.91	5.3	2.99	367.06	0.030	341.24	0.019	1.13
25	7.08	56.05	0.01	0.9	4.25	1	3.97	4	2.98	140.94	0.029	120.77	0.019	2.23
26	6.09	56.05	0.01	0.1	4.39	0.2	3.98	3.2	2.99	6.51	0.036	-21.91	0.018	1.13
27	6.47	56.05	0.01	0.2	4.19	0.3	3.87	3.3	2.94	19.36	0.040	-13.68	0.020	1.27
28	7.03	56.05	0.01	0.3	4.15	0.4	3.84	3.4	2.92	36.46	0.042	2.39	0.021	0.65
29	7.23	56.05	0.01	0.4	4.26	0.5	3.85	2.5	3	60.04	0.049	32.83	0.025	0.67
30	7.78	56.05	0.01	1	4.34	1.1	3.93	4.1	2.84	167.08	0.041	151.46	0.027	0.53
31	7.47	56.05	0.01	1	4.42	1.1	3.97	4.1	2.93	168.63	0.040	145.47	0.022	1.09
32	6.94	56.05	0.01	0.3	4.29	0.4	3.84	3.4	2.9	43.74	0.053	5.87	0.022	0.96
33	6.98	56.05	0.01	0.3	4.03	0.4	3.73	2.4	3	35.66	0.053	-6.88	0.024	0.71
34	7.02	56.05	0.01	0.3	4.18	0.4	3.83	3.4	2.87	39.17	0.046	9.16	0.024	0.71
35	7.25	56.05	0.01	0.4	4.26	0.5	3.86	2.5	3	59.60	0.047	34.31	0.025	0.64
36	7.19	56.05	0.01	0.2	4.39	0.3	3.96	3.3	2.85	25.16	0.039	10.94	0.026	0.31
37	7.35	56.05	0.01	0.6	4.18	0.7	3.82	2.7	2.99	93.27	0.048	65.41	0.026	0.79
38	7.96	56.05	0.01	0.6	4.45	0.7	3.97	3.7	2.85	98.24	0.041	83.33	0.026	0.21
39	7.78	56.05	0.01	0.9	4.15	1	3.82	3	3	144.94	0.046	117.30	0.025	0.46
40	6.85	56.05	0.01	0.3	4.16	0.4	3.82	3.4	2.99	38.55	0.046	-16.09	0.017	1.04
41	5.83	56.05	0.01	0.1	4.33	0.2	3.94	3.2	2.92	5.61	0.038	-17.68	0.022	2.00
42	7.2	56.05	0.01	0.3	4.14	0.4	3.84	3.4	2.94	35.66	0.041	-1.30	0.020	0.43
43	7.16	56.05	0.01	0.3	4.03	0.4	3.73	3.4	2.93	35.66	0.053	-23.45	0.020	0.47
44	7.42	56.05	0.01	0.3	4.09	0.4	3.84	3.4	2.89	30.69	0.036	7.54	0.023	0.22
45	7.42	56.05	0.01	0.7	4.27	0.8	3.89	2.8	3	112.17	0.043	92.01	0.026	0.81
46	7.69	56.05	0.01	0.7	4.47	0.9	3.76	3.9	2.98	116.28	0.040	60.40	0.018	0.45
47	8.12	56.05	0.01	0.8	4.14	0.9	3.84	3.9	2.96	124.87	0.041	83.95	0.019	0.18
48	8.19	56.05	0.01	3.5	4.29	3.6	3.91	6.6	2.89	611.72	0.043	588.75	0.024	0.75
49	8.46	56.05	0.01	2.1	4.16	2.2	3.9	5.2	2.97	352.98	0.033	325.18	0.019	0.23
50	7.99	56.05	0.01	3.2	4.42	3.3	3.94	5.3	3	562.11	0.046	544.17	0.027	1.10
51	7.74	56.05	0.01	1.5	4.08	1.6	3.79	3.6	2.96	248.90	0.046	225.94	0.028	0.86
52	8.3	56.05	0.01	1.3	4.21	1.4	3.9	4.4	2.98	214.87	0.037	180.73	0.019	0.21
53	8.15	56.05	0.01	1.6	4.12	1.7	3.73	3.7	2.98	273.23	0.064	229.24	0.026	0.37
54	8.23	56.05	0.01	1.3	4.15	1.4	3.87	4.4	2.92	212.30	0.037	185.89	0.022	0.24
55	8.03	56.05	0.01	5.1	4.37	5.2	3.96	8.2	2.89	898.57	0.041	880.48	0.025	1.60

Table C15 – Gran alkalinity titration data in Sept 1996

Sample	pH	V_0	C_A	V_1	pH ~ 4.5	V_2	pH ~ 4.0	V_3	pH ~ 3.0	Alk_{Gran1}	Ct_1	Alk_{Gran2}	Ct_2	pCO_2
1	6.84	56.05	0.01	0.9	4.48	1.1	3.99	6.1	2.99	143.59	0.020	105.92	0.012	3.96
2	7.72	56.05	0.01	1.2	4.4	1.4	3.92	6.4	3	196.52	0.023	138.85	0.011	0.71
3	7.41	56.05	0.01	1.5	4.29	1.6	4	8.6	2.94	248.90	0.028	180.30	0.010	1.84
4	6.98	56.05	0.01	1.3	4.24	1.4	4	7.4	2.99	207.85	0.024	145.86	0.010	4.15
5	7.58	56.05	0.01	2.4	4.34	2.7	3.99	14.7	3	385.38	0.011	282.90	0.005	1.93
6	7.36	56.05	0.01	1.2	4.33	1.5	3.93	11.5	3	179.00	0.014	69.17	0.006	1.49
7	6.92	56.05	0.01	0.8	4.3	1	4	13	2.99	107.13	0.014	-9.63	0.005	2.46
8	7.19	56.05	0.01	1	4.49	1.3	3.88	10.3	2.98	161.12	0.019	35.87	0.007	1.98
9	7.46	56.05	0.01	1.6	4.28	1.8	3.96	10.8	3	252.92	0.017	152.81	0.007	1.67
10	8.14	56.05	0.01	2.8	4.41	3.1	3.93	13.1	2.99	473.26	0.016	358.77	0.006	0.65
11	7.72	56.05	0.01	0.9	4.39	1.1	4	11.1	2.96	136.19	0.017	46.12	0.007	0.49
12	7.8	56.05	0.01	1.1	4.2	1.2	3.99	9.2	2.98	167.69	0.023	80.24	0.008	0.51
13	7.42	56.05	0.01	1.1	4.27	1.3	3.89	10.3	2.97	170.90	0.022	45.72	0.007	1.24
14	6.94	56.05	0.01	1.1	4.43	1.2	3.89	4.2	2.89	189.04	0.053	157.90	0.023	4.14
15	7.46	56.05	0.01	4.1	4.29	4.2	3.93	7.2	2.92	717.71	0.040	694.39	0.023	4.74
16	7.71	56.05	0.01	3.4	4.32	3.5	3.89	6.5	2.98	596.08	0.048	553.44	0.019	2.21
17	7.22	56.05	0.01	3.3	4.28	3.4	3.89	6.4	2.96	576.53	0.045	539.20	0.020	6.62
18	7.16	56.05	0.01	4.1	4.35	4.2	3.98	6.2	3	718.26	0.036	709.09	0.028	9.47
19	7.57	56.05	0.01	5	4.48	5.1	3.99	8.1	2.97	883.55	0.042	856.30	0.021	4.53
20	7.45	56.05	0.01	4.8	4.5	4.9	4	7.9	2.99	848.15	0.042	819.25	0.020	5.73
21	7.87	56.05	0.01	1.6	4.36	1.7	4	4.7	2.96	271.68	0.033	252.49	0.020	0.70
22	7.8	56.05	0.01	1.7	4.48	1.8	3.94	4.8	2.99	296.09	0.047	257.23	0.019	0.89
23	7.64	56.05	0.01	1.2	4.41	1.4	3.93	4.4	3	196.52	0.023	182.50	0.018	0.86
24	7.56	56.05	0.01	2.5	4.46	2.7	3.99	5.7	2.97	427.84	0.020	428.22	0.020	2.24
25	6.83	56.05	0.01	1.5	4.49	1.7	3.98	4.7	2.99	251.74	0.021	245.62	0.019	7.10
26	6.03	56.05	0.01	0.2	4.21	0.3	3.92	2.3	2.96	16.97	0.033	11.26	0.029	3.18
27	6.36	56.05	0.01	0.2	4.39	0.3	3.92	2.3	2.99	26.56	0.045	7.86	0.026	2.24
28	7	56.05	0.01	0.3	4.22	0.4	3.85	3.4	2.98	40.29	0.046	-7.26	0.018	0.77
29	7.14	56.05	0.01	0.5	4.41	0.6	3.96	3.6	2.99	79.42	0.040	46.41	0.018	1.10
30	7.61	56.05	0.01	1.3	4.31	1.4	3.99	4.4	2.98	215.61	0.031	194.98	0.019	1.01
31	7.39	56.05	0.01	1.2	4.19	1.3	3.89	4.3	2.97	196.23	0.037	162.90	0.019	1.52
32	6.83	56.05	0.01	0.3	4.47	0.4	3.99	3.4	2.98	44.71	0.039	16.62	0.019	1.26
33	6.93	56.05	0.01	0.3	4.16	0.4	3.82	3.4	2.98	38.55	0.046	-13.78	0.018	0.87
34	6.98	56.05	0.01	0.3	4.3	0.4	3.85	3.4	2.99	43.74	0.051	-9.37	0.018	0.87
35	7.19	56.05	0.01	0.5	4.38	0.6	3.98	3.6	2.98	77.44	0.036	50.88	0.019	0.95
36	7.07	56.05	0.01	0.3	4.06	0.4	3.82	2.4	3	29.44	0.036	10.28	0.025	0.48
37	7.28	56.05	0.01	0.7	4.26	0.8	3.99	3.8	2.99	104.27	0.027	86.55	0.018	1.04
38	7.84	56.05	0.01	0.6	4.45	0.7	3.98	3.7	2.94	97.93	0.039	74.13	0.021	0.27
39	7.8	56.05	0.01	1	4.43	1.1	3.98	4.1	2.99	168.63	0.039	138.61	0.019	0.51
40	6.78	56.05	0.01	0.3	4.28	0.4	3.86	3.4	3	42.61	0.048	-9.37	0.017	1.35
41	6.1	56.05	0.01	0.1	4.46	0.2	3.75	2.2	2.99	13.53	0.081	-36.27	0.025	2.17
42	7.09	56.05	0.01	0.3	4.19	0.4	3.84	3.4	2.94	39.17	0.045	-1.30	0.020	0.61
43	7.08	56.05	0.01	0.3	4.24	0.4	3.92	3.4	2.97	37.20	0.035	7.54	0.019	0.59
44	7.29	56.05	0.01	0.3	4.04	0.4	3.75	3.4	2.93	34.81	0.049	-18.47	0.020	0.34
45	7.31	56.05	0.01	0.9	4.23	1	3.88	4	3	146.21	0.042	101.78	0.018	1.36
46	7.62	56.05	0.01	0.9	4.32	1	3.92	4	2.98	148.80	0.041	112.88	0.019	0.68
47	7.94	56.05	0.01	1	4.45	1.1	3.94	4.1	2.96	170.45	0.045	137.12	0.020	0.37
48	7.97	56.05	0.01	4.6	4.32	4.8	3.96	7.8	2.99	793.21	0.019	795.51	0.020	1.62
49	8.01	56.05	0.01	2.5	4.36	2.7	3.94	5.7	2.97	424.26	0.021	420.95	0.020	0.79
50	7.91	56.05	0.01	3.6	4.45	3.7	3.99	6.7	2.98	632.84	0.040	605.21	0.020	1.48
51	7.47	56.05	0.01	2	4.16	2.1	3.97	5.1	3	324.47	0.022	313.94	0.018	2.09
52	7.99	56.05	0.01	2.1	4.43	2.2	3.96	5.2	2.98	365.55	0.042	333.31	0.019	0.71
53	7.96	56.05	0.01	1.6	4.42	1.7	3.96	4.7	2.99	276.01	0.041	242.60	0.019	0.58
54	8.02	56.05	0.01	1.5	4.3	1.6	4	3.6	3	249.75	0.029	247.28	0.027	0.45
55	7.94	56.05	0.01	5.3	4.47	5.4	3.99	8.4	2.96	936.77	0.042	911.15	0.021	2.05

Table C16 – Gran alkalinity titration data in Nov 1996

Sample	pH	V_0	C_A	V_1	pH ~ 4.5	V_2	pH ~ 4.0	V_3	pH ~ 3.0	Alk_{Gran1}	Ct_1	Alk_{Gran2}	Ct_2	pCO_2
1	6.93	56.05	0.01	0.4	4.44	0.6	3.98	7.6	2.96	52.53	0.019	-8.96	0.009	1.18
2	6.79	56.05	0.01	0.5	4.31	0.7	3.88	7.7	2.97	68.23	0.024	-28.71	0.009	2.11
3	6.78	56.05	0.01	0.6	4.27	0.7	4	5.7	3	86.43	0.026	34.61	0.011	2.74
4	6.76	56.05	0.01	0.5	4.16	0.6	3.93	5.6	3	63.76	0.027	-0.92	0.011	2.12
5	6.95	56.05	0.01	0.7	4.31	0.9	3.87	6.9	2.95	104.66	0.025	29.93	0.010	2.24
6	6.84	56.05	0.01	0.4	4.46	0.6	3.9	6.6	3	57.87	0.026	-30.46	0.009	1.60
7	6.71	56.05	0.01	0.2	4.42	0.3	4	4.3	3	24.77	0.035	-19.97	0.014	0.93
8	7	56.05	0.01	0.5	4.14	0.6	3.91	5.6	2.94	63.76	0.029	9.62	0.013	1.22
9	7.01	56.05	0.01	0.5	4.15	0.6	3.9	5.6	2.95	66.37	0.031	4.50	0.012	1.24
10	7.16	56.05	0.01	1.3	4.34	1.5	3.85	6.5	2.98	214.95	0.028	141.21	0.011	2.83
11	6.86	56.05	0.01	0.3	4.3	0.4	3.98	4.4	3	37.20	0.031	-5.98	0.014	0.98
12	7.18	56.05	0.01	0.6	4.08	0.7	3.85	5.7	2.93	81.60	0.033	14.08	0.013	1.03
13	6.76	56.05	0.01	0.3	4.21	0.4	3.93	4.4	3	33.89	0.032	-16.58	0.013	1.13
14	6.87	56.05	0.01	0.3	4.36	0.4	3.99	4.4	3	40.29	0.033	-4.04	0.014	1.04
15	7.07	56.05	0.01	0.6	4.4	0.8	3.85	4.8	3	93.11	0.029	34.23	0.013	1.51
16	7.12	56.05	0.01	1.1	4.44	1.3	3.96	8.3	2.94	178.68	0.021	115.75	0.010	2.58
17	7.29	56.05	0.01	1	4.15	1.1	3.9	7.1	2.91	155.58	0.032	87.00	0.012	1.52
18	7.32	56.05	0.01	0.9	4.25	1	3.95	6	2.98	142.71	0.032	80.92	0.012	1.30
19	7.08	56.05	0.01	0.9	4.26	1	3.97	6	2.92	141.86	0.030	98.79	0.014	2.25
20	7.04	56.05	0.01	0.9	4.43	1.1	3.81	5.1	2.96	149.36	0.034	87.71	0.015	2.60
21	6.81	56.05	0.01	0.4	4.33	0.6	3.84	5.6	2.98	54.38	0.028	-22.54	0.011	1.61
22	6.99	56.05	0.01	0.6	4.24	0.7	4	6.7	2.96	82.97	0.024	28.66	0.011	1.62
23	6.8	56.05	0.01	0.5	4.38	0.6	3.88	5.6	3	80.98	0.051	-15.91	0.011	2.45
24	7.13	56.05	0.01	0.5	4.08	0.6	3.87	5.6	2.98	60.65	0.029	-12.73	0.011	0.86
25	7.17	56.05	0.01	0.6	4.21	0.7	3.96	5.7	3	84.22	0.027	24.92	0.011	1.09
26	5.72	56.05	0.01	0.2	4.04	0.3	3.85	4.3	2.96	3.34	0.028	-44.06	0.015	1.90
27	6.23	56.05	0.01	0.2	4.15	0.3	3.91	5.3	2.96	11.60	0.030	-48.97	0.012	1.37
28	6.45	56.05	0.01	0.2	4.24	0.3	3.95	5.3	2.84	16.97	0.031	-14.96	0.016	1.17
29	6.49	56.05	0.01	0.2	4.27	0.3	3.94	5.3	2.93	20.06	0.034	-34.44	0.013	1.26
30	7.01	56.05	0.01	0.5	4.21	0.6	3.93	5.6	2.96	69.58	0.032	9.62	0.012	1.30
31	6.92	56.05	0.01	0.5	4.5	0.7	3.88	5.7	2.95	78.00	0.028	16.91	0.012	1.79
32	6.47	56.05	0.01	0.2	4.32	0.3	3.99	5.3	2.94	20.06	0.031	-26.01	0.013	1.32
33	6.57	56.05	0.01	0.2	4.33	0.3	3.96	4.3	2.99	22.45	0.035	-25.81	0.014	1.16
34	6.37	56.05	0.01	0.3	4.08	0.4	3.83	4.4	2.96	30.69	0.037	-31.49	0.014	2.53
35	6.46	56.05	0.01	0.3	4.13	0.4	3.82	4.4	2.93	36.46	0.044	-26.23	0.016	2.43
36	7.09	56.05	0.01	0.3	4.07	0.4	3.83	4.4	2.92	29.44	0.036	-21.27	0.016	0.46
37	6.55	56.05	0.01	0.2	4.5	0.3	4	4.3	2.93	27.45	0.039	-8.09	0.016	1.49
38	6.63	56.05	0.01	0.2	4.41	0.3	3.9	4.3	2.93	27.72	0.049	-25.81	0.016	1.25
39	7.04	56.05	0.01	0.5	4.21	0.6	3.89	4.6	2.94	72.88	0.038	23.50	0.016	1.27
40	6.7	56.05	0.01	0.2	4.11	0.3	3.82	3.3	2.98	16.97	0.042	-31.62	0.018	0.65
41	5.71	56.05	0.01	0.1	4.33	0.2	4	5.2	2.99	2.22	0.030	-52.27	0.011	1.55
42	6.22	56.05	0.01	0.2	4.3	0.3	4	5.3	2.99	17.82	0.028	-34.44	0.011	2.11
43	5.94	56.05	0.01	0.1	4.33	0.2	3.99	4.2	2.98	2.87	0.031	-35.96	0.014	0.88
44	6.45	56.05	0.01	0.2	4.21	0.3	3.94	5.3	2.94	15.07	0.030	-36.70	0.013	1.04
45	6.63	56.05	0.01	0.3	4.34	0.4	4	5.4	2.95	38.55	0.031	-8.18	0.013	1.73
46	6.79	56.05	0.01	0.6	4.13	0.7	3.92	6.7	2.99	78.49	0.026	-2.38	0.010	2.43
47	6.81	56.05	0.01	0.4	4.32	0.5	3.96	4.5	2.93	57.59	0.035	21.07	0.016	1.70
48	7.13	56.05	0.01	1	4.33	1.2	3.85	8.2	2.93	160.84	0.027	64.25	0.010	2.27
49	7.09	56.05	0.01	0.6	4.44	0.8	3.83	5.8	2.92	95.49	0.032	28.99	0.013	1.48
50	7.17	56.05	0.01	0.7	4.22	0.8	3.93	5.8	2.95	106.17	0.033	47.73	0.013	1.37
51	6.92	56.05	0.01	0.5	4.49	0.7	3.85	5.7	2.94	78.65	0.031	11.17	0.013	1.80
52	6.86	56.05	0.01	0.5	4.47	0.7	3.83	4.7	2.98	78.65	0.032	16.41	0.014	2.07
53	6.84	56.05	0.01	0.6	4.2	0.7	3.89	5.7	2.91	89.98	0.037	29.90	0.014	2.48
54	6.89	56.05	0.01	0.5	4.3	0.6	3.97	4.6	2.98	73.58	0.032	31.63	0.014	1.81
55	6.66	56.05	0.01	0.4	4.11	0.5	3.83	4.5	2.95	51.73	0.040	-10.99	0.015	2.16

Table C17 – Gran alkalinity titration data in Jan 1997

Sample	pH	V_0	C_A	V_1	pH ~ 4.5	V_2	pH ~ 4.0	V_3	pH ~ 3.0	Alk_{Gran1}	Ct_1	Alk_{Gran2}	Ct_2	pCO_2
1	6.37	56.05	0.01	0.4	4.46	0.6	3.99	3.6	2.98	53.17	0.019	52.29	0.019	4.36
2	6.77	56.05	0.01	0.6	4.3	0.7	3.89	4.7	2.89	95.72	0.045	51.35	0.018	3.10
3	7.06	56.05	0.01	0.8	4.01	0.9	3.71	3.9	2.83	124.87	0.055	83.95	0.026	2.07
4	6.55	56.05	0.01	0.7	4.28	0.8	3.86	3.8	2.92	113.98	0.049	77.21	0.021	6.13
5	7.05	56.05	0.01	1.2	4.01	1.3	3.71	4.3	2.91	196.23	0.056	137.03	0.021	3.33
6	6.74	56.05	0.01	0.7	4.21	0.8	3.84	3.8	2.97	111.66	0.047	64.07	0.019	3.88
7	5.98	56.05	0.01	0.1	4.5	0.2	3.95	3.2	2.9	10.86	0.045	-13.79	0.023	2.37
8	6.94	56.05	0.01	0.5	4.33	0.6	3.85	3.6	2.91	80.40	0.054	41.54	0.022	1.76
9	6.9	56.05	0.01	0.6	4.49	0.7	3.9	3.7	2.9	100.89	0.053	68.72	0.023	2.42
10	7.37	56.05	0.01	1.8	4.41	1.9	4	4.9	2.98	309.81	0.035	285.53	0.019	2.52
11	6.51	56.05	0.01	0.3	4.5	0.4	3.91	3.4	2.92	47.37	0.052	13.76	0.022	2.81
12	6.9	56.05	0.01	0.7	4.49	0.8	3.95	3.8	2.93	117.68	0.045	89.33	0.021	2.82
13	6.52	56.05	0.01	0.4	4.39	0.5	3.93	4.5	2.96	61.92	0.043	9.85	0.015	3.58
14	6.53	56.05	0.01	0.5	4.14	0.6	3.85	4.6	2.9	70.49	0.039	23.50	0.017	3.98
15	7.42	56.05	0.01	1.4	4.22	1.5	3.83	5.5	2.9	237.55	0.051	179.55	0.017	1.72
16	7.46	56.05	0.01	2	4.41	2.1	3.96	6.1	2.94	347.04	0.041	304.64	0.016	2.29
17	7.38	56.05	0.01	1.4	4.11	1.5	3.79	5.5	2.9	233.45	0.049	169.88	0.017	1.85
18	7.26	56.05	0.01	1.3	4.31	1.4	3.92	5.4	2.92	219.71	0.041	176.18	0.017	2.30
19	7.16	56.05	0.01	1.6	4.22	1.7	3.9	5.7	2.87	269.14	0.038	235.06	0.019	3.55
20	7.01	56.05	0.01	1.6	4.31	1.7	3.88	4.7	2.98	274.94	0.048	230.54	0.019	5.12
21	6.8	56.05	0.01	0.7	4.44	0.8	3.92	3.8	2.99	117.19	0.048	75.49	0.018	3.54
22	7.2	56.05	0.01	0.8	4.45	1	3.74	4	2.95	134.12	0.042	80.92	0.019	1.61
23	6.64	56.05	0.01	0.4	4.38	0.5	3.9	3.5	2.95	62.56	0.048	25.38	0.020	2.74
24	6.96	56.05	0.01	0.5	4.07	0.6	3.72	3.6	2.91	74.85	0.060	14.74	0.021	1.57
25	6.95	56.05	0.01	0.8	4.04	0.9	3.73	3.9	2.94	125.66	0.054	63.09	0.019	2.69
26	5.56	56.05	0.01	0.1	4.3	0.2	3.81	3.2	2.9	9.33	0.059	-35.10	0.022	6.34
27	6.41	56.05	0.01	0.2	4.49	0.3	3.94	3.3	2.93	28.70	0.046	-1.22	0.021	2.16
28	6.55	56.05	0.01	0.3	4.19	0.4	3.84	4.4	2.97	39.17	0.045	-31.49	0.014	2.12
29	6.41	56.05	0.01	0.3	4.28	0.4	3.9	4.4	2.92	40.81	0.041	-5.98	0.016	3.05
30	6.69	56.05	0.01	0.6	4.41	0.7	3.94	4.7	2.93	97.93	0.043	53.20	0.016	3.82
31	6.9	56.05	0.01	0.6	4.06	0.7	3.78	3.7	2.98	87.42	0.045	30.04	0.018	2.10
32	6.19	56.05	0.01	0.3	4.17	0.4	3.84	3.4	2.98	37.90	0.043	-9.37	0.018	4.74
33	6.18	56.05	0.01	0.2	4.33	0.3	3.9	3.3	2.99	25.16	0.045	-17.27	0.018	3.25
34	6.17	56.05	0.01	0.2	4.45	0.3	3.95	3.3	2.99	27.45	0.043	-8.67	0.018	3.62
35	6.41	56.05	0.01	0.3	4.19	0.4	3.83	3.4	2.98	39.75	0.047	-11.54	0.018	2.97
36	6.36	56.05	0.01	0.2	4.5	0.3	3.94	3.3	2.96	28.92	0.047	-5.56	0.020	2.44
37	6.65	56.05	0.01	0.3	4.36	0.4	3.86	3.4	2.96	45.29	0.053	-1.30	0.019	1.94
38	6.58	56.05	0.01	0.3	4.35	0.4	3.88	3.4	2.94	44.40	0.049	5.87	0.020	2.24
39	6.47	56.05	0.01	0.6	4.27	0.7	3.87	3.7	2.93	95.28	0.046	59.38	0.021	6.17
40	6.29	56.05	0.01	0.2	4.18	0.3	3.9	3.3	2.92	16.05	0.034	-5.56	0.021	1.62
41	5.49	56.05	0.01	0.1	4.36	0.2	3.92	3.2	2.94	7.70	0.043	-23.40	0.020	6.74
42	6.02	56.05	0.01	0.1	4.41	0.2	3.96	4.2	2.95	8.06	0.040	-35.96	0.015	1.64
43	5.91	56.05	0.01	0.1	4.49	0.2	3.98	4.2	2.9	9.88	0.041	-24.40	0.017	2.60
44	6.23	56.05	0.01	0.2	4.47	0.3	3.97	4.3	2.91	27.45	0.041	-9.65	0.017	3.15
45	6.6	56.05	0.01	0.4	4.5	0.5	3.99	4.5	2.91	63.41	0.040	29.10	0.017	3.05
46	6.86	56.05	0.01	0.8	4.43	0.9	3.97	4.9	2.91	133.29	0.040	97.35	0.017	3.51
47	6.67	56.05	0.01	0.5	4.48	0.6	4	4.6	2.9	80.40	0.038	49.86	0.018	3.28
48	7.04	56.05	0.01	2	4.31	2.1	3.95	6.1	2.92	343.05	0.037	306.39	0.017	5.96
49	7.01	56.05	0.01	1.1	4.05	1.2	3.79	5.2	2.89	174.57	0.042	118.92	0.017	3.25
50	7.1	56.05	0.01	1.3	4.03	1.4	3.85	5.4	2.9	197.37	0.028	166.14	0.017	2.99
51	7	56.05	0.01	0.9	4.17	1	3.87	4	2.99	142.71	0.038	101.78	0.018	2.72
52	6.81	56.05	0.01	0.9	4.5	1.1	3.79	5.1	2.88	151.97	0.037	103.54	0.018	4.49
53	6.9	56.05	0.01	1.5	4.3	1.6	3.94	5.6	2.92	253.84	0.037	215.48	0.017	6.09
54	6.91	56.05	0.01	1.4	4.48	1.5	4	5.5	2.89	240.97	0.039	211.77	0.018	5.65
55	6.85	56.05	0.01	2.1	4.46	2.2	3.99	6.2	2.98	365.55	0.039	320.68	0.015	9.84

Table C18 – Gran alkalinity titration data in Mar 1997

Sample	pH	V_0	C_A	V_1	pH ~ 4.5	V_2	pH ~ 4.0	V_3	pH ~ 3.0	Alk_{Gran1}	Ct_1	Alk_{Gran2}	Ct_2	pCO_2
1	7.01	56.05	0.01	0.5	4.31	0.6	3.76	2.6	2.99	82.22	0.071	37.03	0.025	1.53
2	6.73	56.05	0.01	0.6	4.15	0.7	3.73	2.7	3	96.13	0.066	46.63	0.024	3.42
3	6.96	56.05	0.01	0.7	4.18	0.8	3.7	2.8	2.96	116.08	0.076	66.63	0.027	2.43
4	6.62	56.05	0.01	0.6	4.1	0.7	3.67	2.7	2.94	96.53	0.076	46.63	0.028	4.42
5	6.89	56.05	0.01	0.8	4.43	0.9	3.85	2.9	3	136.38	0.059	104.18	0.025	3.35
6	7.05	56.05	0.01	0.5	4.24	0.6	3.7	2.6	2.9	81.99	0.080	42.55	0.031	1.39
7	5.89	56.05	0.01	0.2	4.02	0.3	3.73	2.3	2.91	16.97	0.051	-7.56	0.031	4.48
8	6.87	56.05	0.01	0.6	4.01	0.7	3.58	2.7	2.88	96.53	0.094	39.70	0.031	2.48
9	6.94	56.05	0.01	0.5	4.42	0.6	3.81	2.6	2.93	83.42	0.066	54.98	0.030	1.83
10	7.13	56.05	0.01	1.3	4.41	1.4	3.98	3.4	2.96	221.42	0.038	213.50	0.030	3.13
11	6.35	56.05	0.01	0.3	4.48	0.4	3.84	2.4	2.91	48.23	0.063	25.69	0.032	4.14
12	6.48	56.05	0.01	0.6	4.5	0.7	3.88	2.7	2.92	101.43	0.057	82.62	0.032	6.42
13	6.76	56.05	0.01	0.4	4.28	0.5	3.72	2.5	2.86	64.60	0.078	34.31	0.035	2.14
14	6.79	56.05	0.01	0.5	4.2	0.6	3.69	2.6	2.88	81.25	0.080	44.28	0.033	2.51
15	7.07	56.05	0.01	0.7	4.49	0.9	3.64	2.9	2.88	119.04	0.056	88.58	0.032	1.93
16	7.34	56.05	0.01	1.8	4.12	1.9	3.8	4.9	2.99	304.82	0.048	246.55	0.018	2.65
17	7.16	56.05	0.01	1.2	4.26	1.3	3.86	4.3	2.94	202.33	0.048	162.90	0.020	2.67
18	7.02	56.05	0.01	1.3	4.02	1.4	3.66	4.4	2.89	218.16	0.071	146.77	0.022	3.97
19	6.99	56.05	0.01	1.3	4.46	1.4	3.86	4.4	2.9	225.96	0.059	187.51	0.023	4.41
20	6.98	56.05	0.01	1.3	4.41	1.4	3.84	4.4	2.85	225.38	0.061	192.12	0.026	4.50
21	6.76	56.05	0.01	0.6	4.4	0.7	3.92	3.7	2.99	98.24	0.046	57.66	0.018	3.26
22	6.63	56.05	0.01	0.7	4.5	0.9	3.79	3.9	2.99	116.28	0.037	65.70	0.017	5.20
23	6.46	56.05	0.01	0.5	4.39	0.6	3.96	3.6	2.98	78.69	0.039	47.94	0.019	5.22
24	6.73	56.05	0.01	0.5	4.26	0.6	3.85	3.6	2.91	77.88	0.049	41.54	0.022	2.77
25	6.58	56.05	0.01	0.5	4.5	0.6	4	3.6	2.95	80.98	0.039	57.55	0.020	4.07
26	5.24	56.05	0.01	0.1	4.06	0.2	3.79	2.2	2.91	-2.77	0.042	-16.37	0.031	3.27
27	6.02	56.05	0.01	0.2	4.07	0.3	3.74	2.3	3	20.06	0.055	-22.55	0.024	3.82
28	6.13	56.05	0.01	0.2	4.31	0.3	3.79	2.3	2.97	27.98	0.064	-7.56	0.027	4.06
29	6.21	56.05	0.01	0.2	4.5	0.3	3.86	2.3	2.98	30.39	0.060	1.47	0.027	3.64
30	6.75	56.05	0.01	0.6	4.21	0.7	3.77	3.7	2.97	96.90	0.061	30.04	0.018	3.29
31	6.79	56.05	0.01	0.5	4.25	0.6	3.8	2.6	2.95	79.42	0.058	50.67	0.028	2.46
32	6.15	56.05	0.01	0.2	4.46	0.3	3.8	2.3	2.93	30.70	0.070	0.08	0.030	4.23
33	6.03	56.05	0.01	0.2	4.08	0.3	3.65	2.3	2.87	25.16	0.079	-14.58	0.033	4.64
34	6.21	56.05	0.01	0.2	4.19	0.3	3.72	2.3	2.89	26.56	0.071	-5.94	0.032	3.19
35	6.18	56.05	0.01	0.2	4.5	0.3	3.86	2.3	2.94	30.39	0.060	6.65	0.030	3.91
36	6.16	56.05	0.01	0.2	4.03	0.3	3.62	2.3	2.86	24.35	0.083	-18.44	0.034	3.30
37	6.64	56.05	0.01	0.3	4.02	0.4	3.61	2.4	2.84	42.20	0.085	1.36	0.035	1.85
38	6.43	56.05	0.01	0.2	4.16	0.3	3.7	2.3	2.85	26.24	0.074	-2.84	0.036	1.88
39	6.91	56.05	0.01	0.6	4.33	0.7	3.86	3.7	2.98	97.93	0.052	48.28	0.018	2.30
40	5.82	56.05	0.01	0.2	4.02	0.3	3.71	2.3	3	18.62	0.056	-29.25	0.024	5.80
41	5.29	56.05	0.01	0.1	4.11	0.2	3.85	3.2	2.97	-3.84	0.036	-40.89	0.019	1.26
42	6.16	56.05	0.01	0.2	4.14	0.3	3.77	3.3	2.89	22.45	0.055	-23.05	0.022	3.05
43	5.68	56.05	0.01	0.1	4.5	0.2	3.92	3.2	2.97	11.49	0.050	-28.13	0.019	5.40
44	5.86	56.05	0.01	0.2	4.17	0.3	3.81	3.3	2.93	21.90	0.049	-23.05	0.020	6.12
45	6.19	56.05	0.01	0.3	4.24	0.4	3.86	3.4	2.97	40.81	0.045	-3.23	0.019	5.10
46	6.6	56.05	0.01	0.6	4.08	0.7	3.8	3.7	2.98	87.42	0.043	35.03	0.018	4.19
47	6.47	56.05	0.01	0.4	4.02	0.5	3.74	3.5	2.95	51.73	0.049	-8.23	0.019	3.36
48	6.94	56.05	0.01	1.2	4.25	1.3	3.88	4.3	2.96	200.86	0.043	162.90	0.020	4.40
49	6.71	56.05	0.01	0.8	4.32	0.9	3.85	3.9	2.94	133.61	0.053	89.74	0.020	4.97
50	6.85	56.05	0.01	0.5	4.5	0.6	3.98	3.6	2.94	81.51	0.041	56.29	0.021	2.20
51	6.78	56.05	0.01	0.6	4.45	0.7	3.95	3.7	2.93	98.82	0.044	71.50	0.021	3.13
52	6.69	56.05	0.01	0.6	4.48	0.7	3.93	3.7	2.89	100.06	0.048	74.13	0.023	3.90
53	6.68	56.05	0.01	0.5	4.47	0.6	3.91	2.6	3	82.44	0.051	58.93	0.026	3.29
54	6.59	56.05	0.01	0.4	4.3	0.5	3.84	3.5	2.89	61.92	0.053	25.38	0.023	3.04
55	6.74	56.05	0.01	0.4	4.18	0.5	3.78	3.5	2.85	59.60	0.057	21.99	0.025	2.07

C.4 Silica standards

Four standards (200, 400, 600 and 800 μg l^{-1}) and a blank sample (0 μg l^{-1}) were used to calibrate the photospectrometer prior to each sample run. The photospectrometer measured in absorption units, which were converted in micrograms per litre using a calibration curve. The measured value (in adsorption units) for the four standards always ranged between 0.099-0.100 (200 μg l^{-1}), 0.198-0.200 (400 μg l^{-1}), 0.299-0.300 (600 μg l^{-1}) and 0.399-0.400 (800 μg l^{-1}) throughout the sample runs.

C.4 XRF standards

C.4.1 Major Elements

For major elements, two sets of reference materials were used, WS-E (GIT-IWG standard) and OUG94 (internal standard). Comparison between the measured values from reference materials and their actual compositions gives us an indication of the accuracy, precision and consistency of the data (Tables C19 and C20).

Table C19 – Major element data for the WS-E standard for analyses ran between August 1997 and January 1998 on the ARL 8420+ WD XRF
(Units are wt % and the recommended reference composition is in bold)

SiO_2	50.99	51.01	51.02	51.26	51.01	50.89	50.97	50.92	51.09	51.12	**50.70**
TiO_2	2.43	2.42	2.44	2.44	2.44	2.43	2.42	2.43	2.42	2.44	**2.40**
Al_2O_3	13.91	13.92	13.79	13.80	13.90	13.86	13.83	13.92	13.75	13.78	**13.78**
Fe_2O_3	13.23	13.21	13.26	13.24	13.22	13.23	13.23	13.22	13.24	13.21	**13.15**
MnO	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	**0.17**
MgO	5.57	5.62	5.62	5.58	5.58	5.55	5.59	5.60	5.62	5.60	**5.55**
CaO	8.98	9.00	9.04	9.05	9.04	9.04	9.05	9.02	9.04	9.06	**8.95**
Na_2O	2.40	2.45	2.44	2.43	2.41	2.41	2.43	2.40	2.45	2.45	**2.47**
K_2O	0.99	1.01	1.00	1.00	1.00	1.00	1.00	1.00	1.01	1.00	**1.00**
P_2O_5	0.31	0.31	0.31	0.30	0.30	0.31	0.31	0.30	0.31	0.30	**0.30**
Total	99.84	99.96	99.94	100.12	99.92	99.73	99.84	99.84	99.96	99.98	**99.94**

Table C20 – Major element data for the OUG94 standard for analyses ran between August 1997 and January 1998 on the ARL 8420+ WD XRF
(Units are wt % and the recommended reference composition is in bold)

SiO_2	69.72	69.46	69.83	70.10	69.84	69.84	69.80	69.81	69.82	69.92	**69.95**
TiO_2	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.31	0.32	0.32	**0.31**
Al_2O_3	14.66	14.62	14.46	14.52	14.51	14.61	14.60	14.63	14.63	14.65	**14.66**
Fe_2O_3	3.01	3.01	3.02	3.01	3.02	3.03	3.02	3.02	3.02	3.02	**3.05**
MnO	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	**0.08**
MgO	1.05	1.04	1.03	1.04	1.03	1.03	1.04	1.03	1.04	1.03	**1.04**
CaO	1.35	1.35	1.36	1.36	1.37	1.36	1.36	1.36	1.36	1.37	**1.34**
Na_2O	4.63	4.60	4.67	4.67	4.62	4.62	4.60	4.61	4.64	4.65	**4.50**
K_2O	2.97	2.98	2.98	2.96	2.99	2.97	2.97	2.96	2.96	2.98	**2.96**
P_2O_5	0.16	0.17	0.16	0.17	0.16	0.17	0.17	0.17	0.17	0.16	**0.17**
Total	100.01	99.68	99.97	100.28	100.00	100.08	100.02	100.03	100.09	100.24	**100.02**

C.4.1 Trace Elements

Four sets of reference materials were used, BHVO-1, QLO-1, DNC-1 and W-2 (all US Geological Survey standards). A comparison between the measured values from reference materials and actual compositions can be found in Tables C21 to C24.

Table C21 – Trace element data for the BHVO-1 standard for analyses ran between August 1997 and January 1998 on the ARL 8420+ WD XRF
(Units are ppm and the recommended reference composition is in bold)

Rb	10	9	10	11	9	10	9	11	10	10	**11**
Sr	401	401	401	402	401	398	400	404	401	401	**403**
Y	29	29	29	29	29	28	28	29	28	28	**28**
Zr	177	177	177	179	178	176	176	178	176	176	**179**
Ba	146	147	154	150	145	145	154	154	150	157	**139**
Pb	2	2	2	4	4	4	2	2	4	4	**3**
Sc	34	39	34	34	33	36	36	32	35	33	**32**
V	310	310	313	317	322	314	315	320	315	318	**317**
Cr	289	291	290	289	291	292	291	293	289	291	**289**
Co	48	47	48	51	47	48	47	49	49	48	**45**
Ni	121	118	123	122	120	120	120	119	122	120	**121**
Cu	136	141	141	141	142	140	138	139	141	140	**136**
Zn	109	107	109	109	110	107	108	110	110	109	**105**

Table C22 – Trace element data for the QLO-1 standard for analyses ran between August 1997 and January 1998 on the ARL 8420+ WD XRF
(Units are ppm and the recommended reference composition is in bold)

Rb	74	75	75	74	74	74	74	74	74	74	**74**
Sr	333	332	334	333	332	333	335	334	330	332	**336**
Y	25	25	24	25	26	25	25	25	25	25	**24**
Zr	190	189	191	190	191	189	192	191	189	191	**185**
Ba	1379	1374	1372	1376	1362	1366	1398	1381	1378	1384	**1370**
Pb	19	18	18	19	18	17	18	18	18	19	**20**
Sc	8	8	8	7	6	8	7	9	8	8	**9**
V	42	43	48	48	48	53	48	50	50	45	**54**
Cr	4	3	4	5	5	5	6	5	5	5	**3**
Co	9	11	12	11	10	9	11	11	13	12	**7**
Ni	4	5	6	4	5	4	6	4	6	6	**6**
Cu	29	29	29	29	29	28	28	27	28	28	**29**
Zn	61	61	61	61	63	61	62	60	60	61	**61**

Table C23 – Trace element data for the DNC-1 standard for analyses ran between August 1997 and January 1998 on the ARL 8420+ WD XRF
(Units are ppm and the recommended reference composition is in bold)

Rb	4	4	4	5	4	3	4	4	4	4	**5**
Sr	148	147	147	148	147	146	146	147	148	147	**145**
Y	19	19	19	19	20	19	20	19	20	20	**18**
Zr	42	40	40	42	41	41	41	41	41	41	**41**
Ba	115	115	108	111	108	112	114	107	117	113	**114**
Pb	5	6	7	7	7	6	8	7	7	7	**6**
Sc	29	31	32	30	31	32	32	31	28	30	**31**
V	147	143	149	148	147	147	152	149	147	147	**148**
Cr	270	278	274	275	274	276	275	274	274	278	**285**
Co	60	60	63	63	64	61	61	64	65	61	**55**
Ni	249	249	248	252	251	251	250	249	251	251	**247**
Cu	96	96	96	97	96	97	96	96	100	97	**96**
Zn	66	65	68	66	68	68	67	69	66	67	**66**

Table C24 – Trace element data for the W-2 standard for analyses ran between August 1997 and January 1998 on the ARL 8420+ WD XRF
(Units are ppm and the recommended reference composition is in bold)

Rb	20	21	20	22	21	20	21	20	21	21	**20**
Sr	197	199	197	198	197	198	199	198	198	197	**194**
Y	22	23	22	23	22	23	24	23	23	22	**24**
Zr	94	94	95	94	94	93	94	95	94	94	**94**
Ba	178	173	182	181	176	187	177	180	184	176	**182**
Pb	6	7	7	7	8	7	9	11	6	8	**9**
Sc	39	40	38	37	38	36	35	36	39	34	**35**
V	265	253	259	266	263	266	258	265	266	268	**262**
Cr	97	95	96	96	98	97	98	97	95	97	**93**
Co	48	48	52	48	47	51	45	48	48	49	**44**
Ni	69	66	69	69	70	69	66	70	71	68	**70**
Cu	103	104	104	107	107	105	107	106	106	104	**103**
Zn	80	81	77	79	77	80	78	79	81	79	**77**

Looking at the amount of deviation between the actual compositions and the reference material measured values assesses the 'drift' in the data. To take account of this 'drift', the XRF sample data (Appendix E) was recalculated.

APPENDIX D

Water Analysis Data

D.1 Individual Survey chemistry

The following tables (Tables D1 to D6) contain the concentrations of the major ions, alkalinity, silica and pH, as well as discharge, from the individual trips.

Table D1 – Major ion chemistry, alkalinity, silica, pH and discharge data (May 1996)
(Units are $\mu eq\ l^{-1}$ for major ions and alkalinity, $\mu g\ l^{-1}$ for silica, pH units for pH, and $m^{-3}\ sec^{-1}$ for discharge)

Sample	pH	Na	Mg	Ca	K	SBC	Cl	NO3	SO4	F	SAA	Alk	SiO2	Q
Rydal Beck	7.28	96.45	56.35	150.36	0.00	303.16	117.49	20.49	97.84	0.68	235.82	67.34	88	3.38
Stock Ghyll	7.03	212.12	64.11	252.28	2.80	531.31	307.26	25.10	106.54	0.71	438.91	92.40	64	4.81
How Beck	7.21	120.33	61.86	287.16	3.89	473.24	129.70	39.41	121.84	0.70	290.96	182.29	124	0.75
Dale Park Beck	7.31	186.07	70.92	270.19	3.92	531.11	254.40	31.85	151.85	0.74	438.09	93.01	152	2.47
Low Cunsey Beck	7.21	229.58	100.61	505.10	6.27	841.58	343.60	58.11	206.64	1.64	608.35	233.22	144	0.69
Belle Grange Beck	7.26	181.21	63.38	270.17	3.46	518.23	201.17	20.89	177.60	1.84	399.66	118.56	140	0.55
Red Dell Beck	6.98	117.83	74.82	98.20	5.15	296.00	98.86	64.21	120.14	1.33	283.21	12.79	62	3.35
Torver Beck	7.18	112.91	63.88	187.59	3.08	367.46	120.58	29.87	113.11	0.82	263.56	103.90	76	11.28
Washfall Beck	7.21	213.66	94.74	307.73	4.27	620.40	171.92	8.93	130.26	1.11	311.10	309.29	156	0.83
Mill Beck 1	7.06	285.68	153.40	799.64	29.83	1268.6	433.75	320.02	208.55	1.11	962.31	306.24	6	3.38
Stony Beck	7.03	152.61	68.35	142.89	0.00	363.84	99.92	6.91	120.96	0.87	227.79	136.05	40	1.65
Hagg Gill	7.24	93.46	48.65	214.39	1.91	358.41	122.24	21.87	101.98	1.02	246.10	112.31	110	3.73
Trout Beck	6.77	135.54	46.10	174.04	0.00	355.68	92.95	29.42	91.92	1.14	214.29	141.39	64	10.41
Woundale Beck	6.93	157.03	57.20	146.27	0.00	360.49	112.88	9.98	99.31	1.12	222.17	138.32	30	2.05
Hall Gill	6.87	371.28	193.14	377.86	0.00	942.28	148.48	15.78	169.26	1.69	333.52	608.76	64	2.12
Chapel Beck	7.39	180.10	151.44	619.29	16.21	967.04	250.49	128.61	128.54	1.23	507.64	459.41	172	9.31
Chapel Beck Trib	7.38	199.47	116.87	633.93	9.82	960.08	173.31	101.44	141.49	1.04	416.24	543.84	144	0.71
Grayrigg Hall Beck	7.54	243.27	171.03	532.14	23.68	970.12	318.25	57.27	147.42	1.58	522.93	447.18	144	0.59
Flodder Beck	7.19	211.85	134.36	656.68	19.85	1022.7	303.55	156.15	146.96	1.49	606.67	416.08	108	0.13
St Sundays Beck	7.31	347.39	165.45	699.05	13.48	1225.4	354.03	88.54	148.93	1.96	591.51	633.86	112	0.57
Killington Res Trib	6.78	162.91	100.28	307.17	3.45	573.80	223.66	34.16	186.05	1.75	443.88	129.93	188	0.23
River Mint Trib	7.36	160.91	108.02	310.02	4.37	583.32	165.18	14.29	154.48	1.17	333.95	249.37	132	0.82
Borrow Beck	6.84	142.56	70.15	201.52	4.83	419.05	112.46	0.00	127.52	1.13	239.98	179.07	56	14.82
Bannisdale Beck	6.88	213.19	125.15	256.18	4.76	599.28	112.75	4.66	132.76	0.68	250.16	349.12	96	5.60
River Sprint	7.01	74.65	41.58	232.27	3.05	351.55	95.65	25.77	92.27	0.82	213.69	137.86	138	7.99
Moasdale Beck	5.43	119.43	33.51	33.73	4.26	190.93	93.33	32.42	59.91	0.70	185.65	5.28	116	10.49
Castle How Beck	6.09	177.79	63.05	91.44	2.36	334.63	147.95	61.46	112.42	1.13	321.83	12.81	178	1.58
Tarn Beck	6.65	125.64	50.08	81.96	2.17	259.85	109.75	39.41	78.11	0.91	227.27	32.58	30	4.24
Sling Beck	6.64	124.76	52.16	72.10	0.00	249.02	104.53	0.00	87.70	1.09	192.23	56.79	78	2.50
Holehouse Gill	7.06	138.66	75.16	135.56	3.04	352.42	132.02	0.00	75.84	0.86	207.87	144.55	252	2.98
Crosby Gill	7.48	146.68	63.59	156.27	3.75	370.29	135.08	11.15	71.81	0.96	218.04	152.26	58	4.24
Greendale Gill	7.04	160.16	66.48	64.04	2.19	292.87	153.46	21.63	75.52	0.68	250.61	42.26	96	4.63
Nether Beck	6.85	123.71	43.72	61.83	3.00	232.25	115.44	20.86	65.10	1.40	201.41	30.84	76	12.70
Whillan Beck	6.89	117.29	43.14	58.44	2.67	221.54	110.23	16.94	63.37	0.72	190.55	30.99	102	8.29
Hardknott Gill	6.95	101.72	34.96	138.84	1.97	277.49	114.17	22.12	90.20	1.54	226.49	51.00	88	1.84
Whelpside Ghyll	6.84	96.18	29.12	91.28	0.00	216.58	91.12	30.98	71.02	0.59	193.12	23.46	54	1.44
Wyth Burn	6.99	89.66	31.96	117.57	0.00	239.19	70.80	15.43	66.48	1.03	152.71	86.49	28	4.85
Launchy Ghyll	6.98	110.80	28.45	130.79	0.00	270.05	99.88	3.61	65.67	0.42	169.15	100.89	16	2.76
Shoulthwaite Gill	7.49	126.42	44.17	211.46	0.00	382.05	134.77	8.59	99.83	0.93	243.19	138.86	84	2.09
Coledale Beck	6.78	141.41	58.60	181.42	1.88	383.31	176.95	7.05	152.45	2.98	336.45	46.86	80	5.14
Liza Beck	5.75	162.65	60.69	27.44	4.07	254.85	159.08	10.45	65.68	1.56	235.21	19.64	76	10.09
Mill Beck 2	6.65	116.71	50.34	117.99	0.00	285.03	142.05	0.00	90.92	1.20	232.97	52.06	44	3.89
Sour Milk Gill	6.67	148.67	42.69	82.20	0.00	273.57	117.88	32.98	81.57	0.38	232.43	41.14	56	2.82
Styhead Gill	6.78	81.31	31.64	147.75	2.50	263.19	106.09	56.19	77.98	0.60	240.26	22.93	64	7.33
Glenridding Beck	6.98	135.80	57.58	179.91	0.00	373.29	133.80	21.79	98.52	0.52	254.11	119.18	70	6.81
Glencoyne Beck	7.53	99.85	44.88	187.32	0.00	332.05	114.57	12.58	93.26	0.53	220.41	111.64	86	4.27
Aira Beck	7.40	134.19	54.52	171.71	0.00	360.42	152.18	0.00	89.73	0.51	241.91	118.51	102	7.36
Parkhouse Gill	7.69	194.15	150.14	490.64	5.49	840.42	131.74	12.35	125.56	1.96	269.65	570.77	130	1.44
Fusedale Beck	7.68	111.70	74.44	319.74	2.56	508.44	114.34	0.00	89.42	0.89	203.76	304.67	124	4.39
Helvondale Beck	7.92	179.51	155.33	387.47	6.17	728.47	149.35	0.00	50.03	0.79	199.38	529.09	236	4.12
Cawdale Beck	7.60	119.34	72.57	203.39	3.05	398.35	113.90	0.00	59.99	0.47	173.90	224.46	276	3.75
Gatescarth Beck	7.72	93.47	76.19	269.86	0.00	439.52	106.04	22.09	90.83	0.58	218.96	220.56	98	1.74
Naddle Beck	7.59	119.74	76.08	347.21	0.00	543.03	118.87	11.38	136.67	1.02	266.92	276.11	70	3.34
Mosedale Beck	7.48	91.19	82.01	212.95	0.00	386.15	78.68	3.01	76.12	0.43	157.82	228.33	38	4.88
Tailbert Gill	7.47	315.71	221.73	510.19	7.64	1055.3	125.86	0.00	95.92	0.96	221.78	833.50	42	0.44

Table D2 – Major ion chemistry, alkalinity, silica, pH and discharge data (July 1996)

(Units are μeq l^{-1} for major ions and alkalinity, μg l^{-1} for silica, pH units for pH, and m^3 sec^{-1} for discharge)

Sample	pH	Na	Mg	Ca	K	SBC	Cl	NO3	SO4	F	SAA	Alk	SiO2	Q
Rydal Beck	6.99	113.60	55.63	151.29	9.68	330.20	140.11	17.96	85.93	0.80	244.01	76.49	126	1.64
Stock Ghyll	7.81	185.11	88.47	289.62	15.48	578.69	330.55	26.29	97.30	1.20	454.14	129.65	142	0.29
How Beck	7.36	99.48	88.16	312.39	15.41	515.44	140.90	35.97	124.18	1.41	301.05	197.03	216	0.36
Dale Park Beck	7.00	172.30	85.89	305.48	14.79	578.46	266.24	33.55	153.50	0.81	453.30	111.11	226	0.25
Low Cunsey Beck	7.92	203.09	131.17	559.74	22.62	916.62	372.74	38.91	217.82	1.75	629.47	266.74	254	0.31
Belle Grange Beck	7.48	152.15	76.69	321.53	14.06	564.43	205.90	17.69	189.95	1.61	413.54	127.76	166	0.29
Red Dell Beck	7.01	91.02	82.15	119.85	14.12	307.14	99.60	27.67	165.76	1.46	293.04	37.90	88	4.80
Torver Beck	7.38	95.24	80.43	211.42	13.14	400.23	127.66	28.16	116.89	0.93	272.71	89.18	104	5.22
Washfall Beck	7.49	134.95	135.79	381.11	23.87	675.72	157.66	18.28	145.97	1.48	321.90	217.58	162	0.22
Mill Beck 1	8.06	254.39	228.64	854.07	44.56	1381.67	480.36	281.81	233.55	1.27	995.71	400.69	280	0.69
Stony Beck	7.45	78.85	101.12	199.31	17.01	396.28	91.68	19.84	124.17	0.82	235.69	110.53	108	0.46
Hagg Gill	7.81	80.68	60.70	239.10	9.89	390.37	128.33	13.24	113.07	1.33	254.64	131.82	190	1.65
Trout Beck	7.49	82.84	56.72	238.73	9.10	387.40	113.17	11.16	97.40	1.92	221.73	130.01	144	10.16
Woundale Beck	7.85	92.03	81.84	205.51	13.25	392.64	156.45	5.87	67.55	0.68	229.88	146.79	118	1.83
Hall Gill	8.24	94.72	323.11	556.46	52.01	1026.30	140.22	16.04	188.84	1.31	345.10	650.74	248	0.14
Chapel Beck	8.22	185.27	223.97	604.61	39.43	1053.27	277.98	92.88	154.40	1.39	525.26	436.65	254	0.99
Chapel Beck Trib	7.98	161.86	149.23	706.98	27.61	1045.69	164.66	121.71	144.31	1.12	430.69	574.40	212	0.09
Grayrigg Hall Beck	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry
Flodder Beck	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry
St Sundays Beck	7.86	364.11	214.83	717.09	38.60	1334.63	427.95	43.93	140.16	2.25	612.04	683.09	166	0.21
Killington Res Trib	7.18	118.55	118.50	366.43	21.48	624.97	232.42	71.77	155.10	1.30	459.28	196.23	312	0.21
River Mint Trib	7.87	117.35	140.21	351.84	25.94	635.33	176.33	15.54	153.66	1.15	345.54	276.01	204	0.22
Borrow Beck	7.69	82.71	86.79	272.93	14.00	456.42	111.30	9.68	127.33	1.56	248.31	196.23	56	1.09
Bannisdale Beck	7.79	98.53	174.77	351.31	28.11	652.71	110.34	7.63	140.87	2.07	258.85	367.06	230	0.10
River Sprint	7.08	75.55	47.40	255.87	4.07	382.90	97.84	24.94	98.33	0.45	221.11	140.39	170	4.97
Moasdale Beck	6.09	109.51	38.72	53.98	5.74	207.95	117.96	6.51	67.62	0.49	192.10	6.51	144	4.31
Castle How Beck	6.47	108.59	56.01	191.47	8.40	364.47	178.87	36.86	117.26	3.66	333.00	19.36	204	0.50
Tarn Beck	7.03	90.08	62.62	120.83	9.49	283.02	125.77	27.69	81.69	0.75	235.16	36.46	112	3.46
Sling Beck	7.23	96.82	66.41	97.57	10.43	271.23	124.14	10.87	63.89	0.98	198.90	60.04	102	0.23
Holehouse Gill	7.78	89.22	97.78	182.91	13.94	383.85	160.08	0.00	55.00	2.03	215.08	167.08	332	1.07
Crosby Gill	7.47	102.28	83.31	205.84	11.88	403.31	154.76	7.65	63.19	1.09	225.61	168.63	206	1.27
Greendale Gill	6.94	126.29	90.68	89.94	12.08	318.98	173.74	12.82	72.76	1.22	259.31	43.74	246	3.36
Nether Beck	6.98	96.85	57.11	91.21	7.80	252.96	129.26	7.10	72.04	1.50	208.40	35.66	134	5.19
Whillan Beck	7.02	84.29	61.58	87.40	8.03	241.29	129.65	7.56	59.95	1.41	197.16	39.17	154	4.23
Hardknott Gill	7.25	81.43	64.63	148.05	8.12	302.23	125.61	10.71	98.04	1.19	234.35	59.60	188	1.17
Whelpside Ghyll	7.19	74.16	41.72	115.00	5.02	235.89	99.14	18.94	81.75	2.10	199.82	25.16	118	0.50
Wyth Burn	7.35	50.24	39.17	165.18	5.92	260.52	87.52	12.95	57.54	2.12	158.01	93.27	82	0.40
Launchy Ghyll	7.96	67.40	37.11	184.50	5.11	294.13	103.85	7.30	63.87	1.13	175.03	98.24	96	0.49
Shoulthwaite Gill	7.78	86.92	61.89	259.17	8.13	416.12	141.10	15.24	95.29	1.58	251.63	144.94	136	0.40
Coledale Beck	6.85	102.32	134.39	163.32	17.46	417.49	159.23	0.00	188.90	1.48	348.13	38.55	200	2.10
Liza Beck	5.83	140.18	83.71	42.41	11.28	277.57	168.03	7.58	67.76	0.50	243.37	5.61	144	3.36
Mill Beck 2	7.20	102.38	81.66	116.00	10.41	310.45	151.56	0.00	89.50	1.53	241.06	35.66	128	1.20
Sour Milk Gill	7.16	114.55	51.09	125.60	6.72	297.96	157.21	0.00	83.29	1.10	240.50	35.66	90	1.05
Styhead Gill	7.42	84.73	62.70	131.22	8.01	286.66	125.78	21.06	101.76	1.04	248.60	30.69	104	2.14
Glenridding Beck	7.42	83.85	77.79	235.40	9.54	406.58	141.67	20.84	100.42	0.60	262.93	112.17	150	1.34
Glencoyne Beck	7.69	60.04	59.66	234.29	7.67	361.66	115.20	9.99	102.86	1.29	228.06	116.28	164	1.87
Aira Beck	8.12	76.07	76.20	230.75	9.54	392.56	161.68	0.00	88.63	0.52	250.31	124.87	220	0.90
Parkhouse Gill	8.19	145.11	239.94	497.60	32.70	915.36	147.07	20.02	111.92	1.11	279.01	611.72	266	0.35
Fusedale Beck	8.46	83.28	117.42	336.29	16.79	553.77	122.06	0.00	88.77	1.08	210.84	352.98	268	0.60
Heltondale Beck	7.99	110.62	197.29	461.26	24.26	793.42	136.68	0.00	69.62	1.02	206.30	562.11	370	0.71
Cawdale Beck	7.74	80.46	97.56	243.59	12.27	433.87	115.12	0.00	64.81	0.68	179.93	248.90	362	1.77
Gatescarth Beck	8.30	60.30	112.20	292.09	14.12	478.71	116.09	9.79	100.68	0.98	226.56	214.87	156	0.40
Naddle Beck	8.15	90.65	132.12	349.78	18.90	591.45	113.85	18.23	144.11	1.03	276.19	273.23	176	0.57
Mosedale Beck	8.23	49.39	122.46	233.54	15.20	420.58	85.79	0.00	77.51	1.09	163.30	212.30	156	1.06
Tailbert Gill	8.03	132.79	348.38	626.44	41.77	1149.37	131.57	9.77	88.13	1.74	229.48	898.57	326	0.13

Table D3 – Major ion chemistry, alkalinity, silica, pH and discharge data (Sept 1996)

(Units are μeq l^{-1} for major ions and alkalinity, μg l^{-1} for silica, pH units for pH, and m^{-3} sec^{-1} for discharge)

Sample	pH	Na	Mg	Ca	K	SBC	Cl	NO3	SO4	F	SAA	Alk	SiO2	Q
Rydal Beck	6.84	131.55	76.38	191.30	4.03	403.27	133.17	15.53	99.49	0.89	248.19	143.59	114	1.88
Stock Ghyll	7.72	243.02	99.58	247.58	9.63	599.81	284.27	18.45	90.75	0.53	393.46	196.52	136	0.72
How Beck	7.41	123.72	97.91	269.62	8.66	499.91	110.64	28.74	99.18	0.47	238.56	248.90	192	0.31
Dale Park Beck	6.98	232.72	79.37	309.60	10.83	632.52	227.04	31.65	155.59	0.32	414.28	207.85	214	0.24
Low Cunsey Beck	7.58	318.20	131.84	479.50	9.39	938.93	304.22	36.41	193.66	1.00	534.29	385.38	228	0.30
Belle Grange Beck	7.36	164.98	67.24	239.54	9.98	481.74	132.99	12.27	148.53	1.37	293.79	179.00	142	0.25
Red Dell Beck	6.92	193.31	162.28	226.45	14.85	596.89	121.06	20.94	338.12	1.11	480.12	107.13	64	2.73
Torver Beck	7.19	103.94	81.15	196.03	7.15	388.27	99.62	3.85	115.63	0.63	219.09	161.12	94	3.86
Washfall Beck	7.46	110.91	102.02	211.11	4.28	428.33	70.46	7.76	84.55	1.58	162.76	252.92	134	0.09
Mill Beck 1	8.14	315.97	241.20	641.27	41.39	1239.84	354.35	187.54	201.03	0.47	742.92	473.26	264	0.58
Stony Beck	7.72	86.18	71.92	117.74	2.79	278.64	62.18	8.23	65.23	1.74	135.64	136.19	88	0.23
Hagg Gill	7.80	116.68	69.40	191.50	3.81	381.39	98.84	9.11	97.37	0.79	205.32	167.69	168	2.14
Trout Beck	7.42	92.05	50.65	190.40	3.36	336.46	84.16	0.00	72.86	0.79	157.02	170.90	118	4.02
Woundale Beck	6.94	117.60	82.89	176.30	3.81	380.59	128.60	0.00	53.50	2.16	182.10	189.04	70	1.59
Hall Gill	7.46	172.37	311.05	495.14	9.88	988.44	108.81	7.10	133.29	0.37	249.20	717.71	218	0.13
Chapel Beck	7.71	275.78	292.73	464.56	10.44	1043.50	215.96	67.85	133.80	0.68	417.62	596.08	248	0.92
Chapel Beck Trib	7.22	232.42	186.80	455.41	8.83	883.46	112.15	68.70	103.02	0.63	283.87	576.53	204	0.06
Grayrigg Hall Beck	7.16	254.76	406.60	597.02	12.71	1271.10	302.54	42.50	179.07	0.89	524.11	718.26	162	0.06
Flodder Beck	7.57	264.70	327.43	647.19	12.52	1251.83	199.87	38.37	103.54	0.95	341.78	883.55	94	0.12
St Sundays Beck	7.45	404.57	239.94	701.78	13.60	1359.88	320.60	44.47	129.70	0.84	494.77	848.15	172	0.22
Killington Res Trib	7.87	201.80	173.29	352.47	7.35	734.91	216.88	44.50	188.26	0.79	449.64	271.68	294	0.39
River Mint Trib	7.80	176.02	204.90	307.49	6.95	695.37	197.18	0.00	187.29	0.63	384.48	296.09	188	0.39
Borrow Beck	7.64	111.22	109.41	293.78	5.20	519.61	134.73	0.00	178.53	1.00	313.26	196.52	92	0.63
Bannisdale Beck	7.56	145.99	209.03	287.06	6.49	648.56	88.16	0.00	111.18	0.79	199.33	427.84	192	0.18
River Sprint	6.83	105.48	84.36	253.00	4.47	447.31	80.19	13.75	89.05	0.58	182.98	251.74	178	2.49
Moasdale Beck	6.03	128.16	37.29	54.58	2.22	222.26	113.16	2.85	71.47	0.37	187.47	16.97	128	4.39
Castle How Beck	6.36	162.07	60.66	146.63	3.73	373.09	173.30	19.22	131.43	0.74	323.95	26.56	182	0.29
Tarn Beck	7.00	138.76	64.34	83.23	2.89	289.22	109.29	32.33	77.09	0.63	218.71	40.29	104	2.78
Sling Beck	7.14	115.41	72.73	104.55	2.96	295.64	124.57	0.00	55.90	0.74	180.48	79.42	90	0.25
Holehouse Gill	7.61	139.07	123.08	188.98	4.56	455.68	155.10	0.00	52.63	0.89	207.73	215.61	296	1.08
Crosby Gill	7.39	144.99	89.98	154.67	3.94	393.58	131.22	0.00	56.31	0.58	187.53	196.23	212	1.07
Greendale Gill	6.83	165.75	82.77	69.12	3.21	320.85	158.80	13.85	74.42	1.68	247.07	44.71	214	2.16
Nether Beck	6.93	132.00	54.51	89.03	2.78	278.33	136.11	0.00	90.17	0.53	226.28	38.55	124	4.77
Whillan Beck	6.98	139.80	78.06	102.29	3.23	323.38	166.36	7.66	76.32	0.63	250.34	43.74	138	2.46
Hardknott Gill	7.19	155.93	52.70	139.31	3.51	351.46	131.72	10.61	115.43	1.74	257.75	77.44	182	0.97
Whelpside Ghyll	7.07	123.54	45.70	149.54	3.22	322.00	69.50	11.29	177.91	0.68	258.70	29.44	108	0.30
Wyth Burn	7.28	84.57	40.99	151.68	2.80	280.05	77.77	0.00	61.51	0.42	139.28	104.27	74	0.43
Launchy Ghyll	7.84	74.35	35.17	171.67	6.37	287.56	101.68	0.00	65.43	0.47	167.11	97.93	72	0.64
Shoulthwaite Gill	7.80	135.11	69.75	261.59	4.71	471.17	153.47	15.00	109.95	0.58	278.43	168.63	124	0.39
Coledale Beck	6.78	155.24	126.18	168.30	4.54	454.25	152.59	0.00	252.66	1.26	405.25	42.61	212	1.32
Liza Beck	6.10	183.85	81.60	42.38	3.11	310.93	183.56	6.33	90.60	0.79	280.49	13.53	132	4.24
Mill Beck 2	7.09	140.83	78.22	110.98	3.33	333.36	159.62	0.00	116.94	0.84	276.57	39.17	124	1.06
Sour Milk Gill	7.08	133.17	44.75	120.11	3.01	301.04	155.01	0.00	84.65	0.68	239.66	37.20	78	0.57
Styhead Gill	7.29	124.76	62.15	134.43	3.25	324.59	126.69	24.48	115.98	0.68	267.16	34.81	92	1.39
Glenridding Beck	7.31	111.21	69.20	217.67	4.02	402.10	124.86	12.71	96.38	1.05	233.96	146.21	136	2.96
Glencoyne Beck	7.62	93.97	59.74	229.07	3.87	386.65	99.15	0.00	101.49	1.42	200.64	148.80	148	1.71
Aira Beck	7.94	114.81	70.92	223.01	4.13	412.87	140.03	0.00	76.82	0.47	216.85	170.45	212	1.03
Parkhouse Gill	7.97	215.39	244.64	601.44	10.72	1072.19	129.15	16.04	94.11	1.84	239.31	793.21	258	0.37
Fusedale Beck	8.01	114.53	136.14	373.00	6.30	629.98	97.41	0.00	87.09	0.79	184.50	424.26	254	0.64
Helvondale Beck	7.91	171.54	194.91	437.61	8.12	812.19	93.79	0.00	53.92	0.58	147.71	632.84	328	0.76
Cawdale Beck	7.47	137.85	105.55	255.47	5.04	503.92	103.31	0.00	59.91	0.32	163.22	324.47	316	1.59
Gatescarth Beck	7.99	108.19	117.98	349.79	5.82	581.77	98.20	5.46	94.29	0.42	197.95	365.55	138	0.42
Naddle Beck	7.96	85.04	117.12	341.68	5.49	549.33	107.76	7.59	144.15	0.84	259.51	276.01	168	0.31
Mosedale Beck	8.02	59.83	96.02	254.31	6.78	416.95	74.64	0.00	80.06	0.47	154.70	249.75	156	0.84
Tailbert Gill	7.94	187.44	300.88	644.94	11.45	1144.70	107.03	0.00	82.17	0.47	189.20	936.77	320	0.10

Table D4 – Major ion chemistry, alkalinity, silica, pH and discharge data (Nov 1996)

(Units are μeq l^{-1} for major ions and alkalinity, μg l^{-1} for silica, pH units for pH, and m^{-3} sec^{-1} for discharge)

Sample	pH	Na	Mg	Ca	K	SBC	Cl	NO3	SO4	F	SAA	Alk	SiO2	Q
Rydal Beck	6.93	80.36	46.95	125.27	1.77	254.35	104.11	9.32	70.22	0.75	183.64	52.53	182	10.13
Stock Ghyll	6.79	157.81	47.69	187.69	4.85	398.05	205.96	22.80	76.97	1.00	305.73	68.23	162	6.33
How Beck	6.78	67.07	34.48	160.07	4.02	265.65	78.93	19.54	51.89	1.34	150.36	86.43	212	0.33
Dale Park Beck	6.76	128.76	49.08	186.97	5.28	370.09	152.54	31.84	99.45	1.24	283.83	63.76	292	3.09
Low Cunsey Beck	6.95	96.59	42.33	212.50	5.12	356.54	135.22	23.50	79.96	1.33	238.68	104.66	254	1.19
Belle Grange Beck	6.84	95.07	33.25	141.75	3.72	273.79	115.96	0.00	79.97	1.66	195.94	57.87	254	0.66
Red Dell Beck	6.71	101.04	64.17	84.21	6.19	255.61	94.55	16.54	110.24	1.25	221.33	24.77	164	3.58
Torver Beck	7.00	77.62	43.91	128.96	3.89	254.38	91.11	10.83	66.98	0.95	168.92	63.76	176	12.51
Washfall Beck	7.01	55.62	24.66	80.11	2.24	162.64	50.27	0.00	24.13	1.15	74.40	66.37	156	0.64
Mill Beck 1	7.16	183.08	98.31	512.47	24.81	818.66	262.60	175.45	137.93	1.01	575.99	214.95	244	3.06
Stony Beck	6.86	75.39	33.76	70.59	1.26	181.00	72.68	0.00	31.72	1.11	104.40	37.20	110	0.54
Hagg Gill	7.18	77.41	40.30	177.57	3.66	298.94	95.15	16.17	78.43	0.98	189.75	81.60	176	7.04
Trout Beck	6.76	62.82	21.37	80.66	1.15	166.00	60.29	4.67	27.04	1.19	92.00	33.89	120	27.14
Woundale Beck	6.87	81.47	29.67	75.88	1.31	188.33	78.17	2.57	26.13	0.66	106.87	40.29	112	8.69
Hall Gill	7.07	70.62	36.74	71.87	1.25	180.48	37.88	2.03	17.11	1.88	57.02	93.11	166	2.38
Chapel Beck	7.12	77.77	65.39	267.40	9.92	420.48	90.34	57.04	54.41	1.67	201.80	178.68	290	12.15
Chapel Beck Trib	7.29	64.52	37.80	205.04	5.35	312.71	54.05	26.34	42.28	1.49	122.68	155.58	246	1.10
Grayrigg Hall Beck	7.32	85.89	60.39	187.88	10.76	344.91	97.72	27.55	44.92	1.52	170.19	142.71	242	2.20
Flodder Beck	7.08	53.87	34.16	166.97	6.87	261.87	43.74	27.11	17.91	1.77	88.76	141.86	238	1.86
St Sundays Beck	7.04	91.72	43.68	184.56	5.82	325.79	77.58	21.69	43.90	1.54	143.17	149.36	246	2.43
Killington Res Trib	6.81	73.14	45.02	137.90	3.35	259.41	121.39	13.64	51.20	1.49	186.23	54.38	238	0.76
River Mint Trib	6.99	87.26	58.58	168.12	4.59	318.54	123.71	9.32	74.41	1.38	207.44	82.97	220	2.34
Borrow Beck	6.80	125.84	61.92	177.89	6.85	372.50	186.08	0.00	77.55	0.38	263.63	80.98	154	9.25
Bannisdale Beck	7.13	71.42	41.93	85.82	3.00	202.17	49.82	0.00	26.37	1.13	76.19	60.65	170	2.30
River Sprint	7.17	46.32	25.80	144.11	3.42	219.64	59.70	8.66	39.23	0.78	107.58	84.22	204	5.70
Moasdale Beck	5.72	82.40	23.12	23.27	3.86	132.66	76.77	5.77	37.88	1.01	120.42	3.34	170	6.81
Castle How Beck	6.23	162.12	57.49	83.38	4.29	307.27	184.04	18.53	78.81	1.71	281.38	11.60	212	1.36
Tarn Beck	6.45	93.39	37.22	60.92	2.97	194.50	96.79	11.58	50.03	1.06	158.41	16.97	158	5.63
Sling Beck	6.49	70.05	29.29	40.48	0.98	140.80	76.45	0.00	24.40	0.54	100.86	20.06	136	2.76
Holehouse Gill	7.01	79.12	42.88	77.35	3.14	202.50	83.48	0.00	26.29	0.83	109.77	69.58	350	2.85
Crosby Gill	6.92	94.12	40.80	100.27	4.07	239.27	94.23	4.80	36.21	1.02	135.24	78.00	222	6.06
Greendale Gill	6.47	211.98	87.98	84.75	5.62	390.33	247.47	8.91	94.39	0.68	350.77	20.06	204	4.64
Nether Beck	6.57	184.99	65.37	92.46	6.92	349.75	210.86	10.06	85.13	0.70	306.06	22.45	136	12.34
Whillan Beck	6.37	185.90	68.37	92.63	6.69	353.60	209.37	3.51	81.87	1.47	294.74	30.69	126	10.64
Hardknott Gill	6.46	120.16	41.30	164.01	4.62	330.09	165.01	4.35	91.45	0.60	260.81	36.46	164	2.02
Whelpside Ghyll	7.09	186.09	56.34	176.60	2.93	421.96	207.59	27.18	130.16	1.39	364.93	29.44	140	1.97
Wyth Burn	6.55	69.97	24.94	91.74	1.31	187.96	77.79	0.00	32.85	0.68	110.63	27.45	96	8.11
Launchy Ghyll	6.63	66.97	17.20	79.05	1.14	164.36	83.80	0.00	28.47	0.53	112.27	27.72	94	5.50
Shoulthwaite Gill	7.04	105.18	36.75	175.94	2.23	320.09	158.09	0.00	64.11	1.10	222.20	72.88	170	3.86
Coledale Beck	6.70	161.13	66.78	206.72	5.19	439.82	247.08	0.00	158.50	0.79	405.58	16.97	170	9.42
Liza Beck	5.71	75.49	28.17	12.74	2.72	119.11	76.33	3.40	31.34	0.53	111.06	2.22	132	13.34
Mill Beck 2	6.22	98.40	42.44	99.47	1.68	241.98	131.89	0.00	75.67	1.21	207.56	17.82	148	6.65
Sour Milk Gill	5.94	76.18	21.88	42.12	0.98	141.16	85.34	2.87	27.99	0.24	116.20	2.87	96	3.41
Styhead Gill	6.45	43.13	16.78	78.38	2.30	140.60	82.71	6.81	30.13	0.36	119.64	15.07	102	8.22
Glenridding Beck	6.63	61.24	25.96	81.13	1.18	169.50	73.11	5.84	36.98	1.30	115.92	38.55	140	10.29
Glencoyne Beck	6.79	80.92	36.37	151.80	1.88	270.97	104.29	0.00	61.78	0.26	166.08	78.49	186	5.63
Aira Beck	6.81	74.91	30.43	95.85	1.41	202.60	90.66	0.00	34.95	0.64	125.61	57.59	218	7.71
Parkhouse Gill	7.13	57.39	44.38	145.02	3.36	250.14	44.46	3.61	23.00	1.41	71.07	160.84	296	2.18
Fusedale Beck	7.09	43.25	28.82	123.81	2.37	198.25	46.01	0.00	25.53	0.55	71.54	95.49	316	6.79
Heltondale Beck	7.17	45.21	39.12	97.59	2.84	184.77	29.85	0.00	14.28	0.89	44.13	106.17	348	9.67
Cawdale Beck	6.92	51.37	31.24	87.54	2.51	172.66	43.66	2.93	21.64	0.36	68.23	78.65	328	5.91
Gatescarth Beck	6.86	37.60	30.65	108.56	1.24	178.05	41.44	4.05	28.09	0.88	73.59	78.65	202	1.80
Naddle Beck	6.84	59.80	38.00	173.42	1.90	273.12	96.95	0.00	56.17	1.64	153.12	89.98	166	4.34
Mosedale Beck	6.89	41.51	37.33	96.93	1.23	177.01	55.00	0.00	24.20	0.82	79.20	73.58	180	4.36
Tailbert Gill	6.66	75.07	52.73	121.32	3.57	252.69	38.62	0.00	17.15	1.28	55.77	51.73	198	0.51

Table D5 – Major ion chemistry, alkalinity, silica, pH and discharge data (Jan 1997)

(Units are μeq l^{-1} for major ions and alkalinity, μg l^{-1} for silica, pH units for pH, and m^{-3} sec^{-1} for discharge)

Sample	pH	Na	Mg	Ca	K	SBC	Cl	NO3	SO4	F	SAA	Alk	SiO2	Q
Rydal Beck	6.37	87.80	48.93	130.82	0.00	267.55	105.83	9.47	71.38	0.89	186.68	53.17	178	5.46
Stock Ghyll	6.77	187.69	53.96	214.55	2.42	458.61	229.41	25.40	85.73	0.53	340.54	95.72	168	5.59
How Beck	7.06	76.43	36.94	173.47	2.38	289.22	82.85	20.51	54.47	0.47	157.83	124.87	216	0.72
Dale Park Beck	6.55	158.19	57.31	220.25	3.24	438.99	174.92	36.52	114.04	0.32	325.47	113.98	276	1.08
Low Cunsey Beck	7.05	121.75	50.18	255.37	3.21	430.50	157.69	27.40	93.24	1.00	278.33	196.23	252	0.65
Belle Grange Beck	6.74	132.96	44.10	190.13	2.47	369.66	151.30	0.00	104.34	1.37	255.64	111.66	258	0.39
Red Dell Beck	5.98	121.94	74.64	97.04	5.20	298.82	106.91	18.70	124.66	1.11	250.27	10.86	158	2.24
Torver Beck	6.94	93.93	50.58	149.07	2.48	296.06	102.41	12.17	75.29	0.63	189.87	80.40	168	10.26
Washfall Beck	6.9	73.98	31.25	102.09	1.44	208.76	62.01	0.00	29.76	1.58	91.77	100.89	154	0.64
Mill Beck 1	7.37	210.95	105.76	559.08	21.09	896.89	277.97	185.72	146.01	0.47	609.70	309.81	248	0.61
Stony Beck	6.51	91.67	39.46	82.34	0.00	213.48	82.66	0.00	36.08	1.74	118.74	47.37	106	0.75
Hagg Gill	6.9	103.22	50.60	225.37	2.03	381.22	117.13	19.91	96.55	0.79	233.60	117.68	170	4.13
Trout Beck	6.52	66.78	21.62	82.36	0.00	170.76	59.78	4.63	26.81	0.79	91.22	61.92	122	8.23
Woundale Beck	6.53	89.32	31.20	79.93	0.00	200.46	80.22	2.63	26.81	1.16	109.67	70.49	114	2.81
Hall Gill	7.42	94.76	47.37	92.41	0.00	234.54	46.89	2.51	21.18	0.37	70.59	237.55	174	0.39
Chapel Beck	7.46	100.16	78.40	323.29	8.56	510.41	105.48	66.60	63.53	0.68	235.61	347.04	282	3.04
Chapel Beck Trib	7.38	84.23	45.93	252.69	3.95	386.81	64.05	31.22	50.11	0.63	145.38	233.45	254	0.55
Grayrigg Hall Beck	7.26	115.23	76.59	239.31	10.79	441.92	120.48	33.97	55.38	0.89	209.83	219.71	244	0.43
Flodder Beck	7.16	66.09	39.07	193.31	5.91	304.38	48.53	30.09	19.87	0.95	98.49	269.14	242	0.23
St Sundays Beck	7.01	120.25	54.09	230.86	4.51	409.69	93.68	26.20	53.02	0.84	172.90	274.94	248	0.71
Killington Res Trib	6.8	99.68	58.25	179.18	2.04	339.15	153.36	17.23	64.69	0.79	235.28	117.19	254	0.27
River Mint Trib	7.2	118.31	75.41	217.08	3.10	413.90	155.21	11.69	93.36	0.63	260.26	134.12	218	0.70
Borrow Beck	6.64	134.65	63.22	182.22	4.43	384.52	185.60	0.00	77.35	1.00	262.96	62.56	150	6.90
Bannisdale Beck	6.96	80.55	45.33	92.60	1.75	220.24	51.95	0.00	27.50	0.79	79.44	74.85	168	1.97
River Sprint	6.95	67.15	34.82	197.42	2.62	302.01	78.97	11.45	51.90	0.58	142.33	125.66	198	2.82
Moasdale Beck	5.56	95.36	25.88	25.46	3.35	150.05	84.00	6.32	41.45	0.37	131.76	9.33	172	5.75
Castle How Beck	6.41	190.26	65.17	93.58	2.48	351.49	203.66	20.51	87.21	0.74	311.38	28.70	208	1.01
Tarn Beck	6.55	108.92	41.87	68.06	1.85	220.70	106.21	12.71	54.90	0.63	173.82	39.17	152	3.21
Sling Beck	6.41	96.07	38.82	53.12	0.00	188.00	98.65	0.00	31.49	0.74	130.14	40.81	128	2.77
Holehouse Gill	6.69	106.02	55.25	99.24	2.27	262.77	104.38	0.00	32.88	0.89	137.26	97.93	342	1.36
Crosby Gill	6.9	100.43	41.72	102.63	2.51	247.30	93.90	4.78	36.08	0.58	134.76	87.42	232	2.75
Greendale Gill	6.19	257.10	103.41	97.72	3.46	461.68	283.15	10.19	108.00	1.68	401.34	37.90	202	2.41
Nether Beck	6.18	222.76	76.04	106.41	5.30	410.50	239.40	11.43	96.65	0.53	347.48	25.16	128	9.40
Whillan Beck	6.17	221.06	78.56	105.23	4.94	409.80	234.68	3.93	91.76	0.63	330.36	27.45	124	4.68
Hardknott Gill	6.41	136.40	44.55	178.69	2.57	362.21	175.07	4.62	97.02	1.74	276.71	39.75	162	0.87
Whelpside Ghyll	6.36	219.23	63.47	200.08	0.00	482.78	229.74	30.08	144.05	0.68	403.86	28.92	138	0.83
Wyth Burn	6.65	85.43	28.99	107.55	0.00	221.97	88.61	0.00	37.42	0.42	126.03	45.29	78	3.29
Launchy Ghyll	6.58	85.13	20.73	96.68	0.00	202.54	99.75	0.00	33.89	0.47	133.65	44.40	84	1.21
Shoulthwaite Gill	6.47	131.71	43.51	211.16	0.00	386.38	184.36	0.00	74.77	0.58	259.13	95.28	172	1.01
Coledale Beck	6.29	183.10	72.43	225.33	2.36	483.22	262.62	0.00	168.47	1.26	431.09	16.05	178	0.08
Liza Beck	5.49	131.21	47.59	20.38	3.23	202.41	125.49	5.58	51.52	0.79	182.59	7.70	128	5.13
Mill Beck 2	6.02	116.59	48.25	113.11	0.00	277.95	146.53	0.00	84.07	0.84	230.60	8.06	146	1.83
Sour Milk Gill	5.91	92.68	25.63	49.14	0.00	167.46	97.91	3.29	32.11	0.68	133.31	9.88	94	2.03
Styhead Gill	6.23	64.73	23.79	112.52	1.92	202.96	115.48	9.51	42.06	0.68	167.05	27.45	106	6.21
Glenridding Beck	6.6	92.90	37.59	118.04	0.00	248.53	103.55	8.27	52.37	1.05	164.19	63.41	144	3.61
Glencoyne Beck	6.86	102.63	43.65	184.02	0.00	330.30	122.68	0.00	72.68	0.42	195.36	133.29	182	2.28
Aira Beck	6.67	99.78	38.69	122.51	0.00	260.98	112.71	0.00	43.45	0.47	156.16	80.40	208	7.30
Parkhouse Gill	7.04	68.30	49.78	163.46	1.85	283.38	47.83	3.89	24.74	0.84	76.46	343.05	292	0.88
Fusedale Beck	7.01	54.86	34.25	148.52	1.20	238.84	53.00	0.00	29.41	0.79	82.41	174.57	320	2.97
Heltondale Beck	7.1	56.66	46.45	115.98	1.87	220.95	33.68	0.00	16.11	0.58	49.78	197.37	356	1.20
Cawdale Beck	7	66.84	38.68	108.71	1.65	215.88	52.30	3.51	25.93	0.32	81.75	142.71	340	1.33
Gatescarth Beck	6.81	54.59	41.76	148.81	0.00	245.16	54.73	5.35	37.10	0.42	97.18	151.97	200	1.44
Naddle Beck	6.9	82.79	49.24	227.13	0.00	359.16	122.91	0.00	71.21	0.84	194.11	253.84	172	2.95
Mosedale Beck	6.91	62.57	53.22	138.40	0.00	254.20	75.88	0.00	33.39	0.47	109.27	240.97	168	4.93
Tailbert Gill	6.85	103.23	69.16	159.09	2.42	333.90	47.98	0.00	21.31	0.47	69.28	365.55	202	0.34

Table D6 – Major ion chemistry, alkalinity, silica, pH and discharge data (Mar 1997)

(Units are μeq l^{-1} for major ions and alkalinity, μg l^{-1} for silica, pH units for pH, and m^3 sec^{-1} for discharge)

Sample	pH	Na	Mg	Ca	K	SBC	Cl	NO3	SO4	F	SAA	Alk	SiO2	Q
Rydal Beck	7.01	112.23	55.08	155.04	0.00	322.35	130.77	11.77	89.36	0.58	231.90	82.22	180	7.56
Stock Ghyll	6.73	193.49	47.63	207.27	2.38	450.77	231.39	25.73	87.89	0.70	345.02	96.13	166	4.90
How Beck	6.96	83.18	33.86	173.18	2.41	292.64	86.10	21.43	57.42	1.57	164.95	116.08	214	0.35
Dale Park Beck	6.62	171.31	53.39	222.38	3.32	450.40	183.96	38.62	121.64	1.70	344.21	96.53	284	1.09
Low Cunsey Beck	6.89	136.38	47.09	263.57	3.36	450.41	169.28	29.58	101.53	0.87	300.39	136.38	254	0.56
Belle Grange Beck	7.05	119.35	33.73	159.17	2.10	314.34	131.99	0.00	92.16	1.18	224.15	81.99	256	0.21
Red Dell Beck	5.89	95.40	52.99	70.59	3.88	222.87	81.58	14.37	96.38	0.43	192.32	16.97	160	2.61
Torver Beck	6.87	105.82	49.84	155.46	2.63	313.75	111.33	13.30	82.93	0.72	207.57	96.53	172	9.36
Washfall Beck	6.94	63.05	23.19	81.01	1.16	168.41	51.57	0.00	25.09	0.72	76.65	83.42	154	0.51
Mill Beck 1	7.13	207.90	86.29	501.30	19.16	814.65	258.66	173.96	138.47	0.52	571.09	221.42	246	0.77
Stony Beck	6.35	66.22	25.47	55.65	0.00	147.34	58.67	0.00	25.97	0.72	84.64	48.23	108	0.69
Hagg Gill	6.48	88.23	36.64	176.97	1.62	303.45	95.64	16.36	79.89	0.61	191.88	101.43	174	4.97
Trout Beck	6.76	77.03	21.48	88.89	0.00	187.40	67.46	5.25	30.71	1.99	103.42	64.60	120	8.11
Woundale Beck	6.79	113.07	34.89	94.89	0.00	242.85	99.97	3.30	33.96	0.67	137.23	81.25	114	2.56
Hall Gill	7.07	102.10	45.74	92.95	0.00	240.80	72.64	3.91	33.30	1.20	109.85	119.04	170	0.49
Chapel Beck	7.34	138.81	90.90	401.44	10.76	641.91	136.34	86.67	83.59	1.43	306.61	304.82	286	2.99
Chapel Beck Trib	7.16	86.76	38.94	235.46	3.73	364.89	62.28	30.56	49.49	0.97	142.33	202.33	250	0.69
Grayrigg Hall Beck	7.02	132.41	76.07	251.62	11.51	471.61	132.31	37.50	61.83	1.16	231.63	218.16	244	0.65
Flodder Beck	6.99	89.11	43.73	235.63	7.29	375.77	61.97	38.65	25.90	1.00	126.53	225.96	240	0.54
St Sundays Beck	6.98	138.10	52.87	244.70	4.84	440.51	103.78	29.18	59.63	1.16	192.59	225.38	248	0.87
Killington Res Trib	6.76	119.16	60.64	197.51	2.28	379.59	176.18	19.88	75.47	1.35	271.53	98.24	246	0.32
River Mint Trib	6.63	111.38	61.97	188.08	2.73	364.16	140.18	10.61	85.46	0.96	236.25	116.28	220	0.73
Borrow Beck	6.46	108.68	44.74	136.78	3.38	293.60	145.51	0.00	61.53	0.18	207.04	78.69	152	7.78
Bannisdale Beck	6.73	91.41	45.94	97.75	1.88	236.98	98.49	0.00	52.83	1.01	151.31	77.88	170	1.37
River Sprint	6.58	66.36	28.28	176.80	2.38	273.81	101.95	14.87	67.92	0.38	184.74	80.98	202	2.89
Moasdale Beck	5.24	114.03	27.92	28.12	3.88	173.95	99.85	7.54	49.98	0.82	157.38	-2.77	172	6.48
Castle How Beck	6.02	232.12	71.71	106.80	2.91	413.55	245.74	24.86	106.85	0.48	377.45	20.06	210	1.20
Tarn Beck	6.13	137.34	47.53	80.34	2.24	267.44	131.98	15.87	69.21	0.87	217.07	27.98	156	3.35
Sling Beck	6.21	101.49	37.17	52.47	0.00	191.13	103.01	0.00	33.42	0.92	136.42	30.39	132	2.86
Holehouse Gill	6.75	134.50	62.97	117.41	2.74	317.61	129.86	0.00	41.58	0.58	171.44	96.90	346	1.84
Crosby Gill	6.79	120.17	44.20	114.78	2.86	282.00	110.13	5.63	42.97	0.52	158.73	79.42	224	3.07
Greendale Gill	6.15	288.48	106.00	101.84	3.75	500.07	314.64	11.37	121.87	0.52	447.88	30.70	204	2.67
Nether Beck	6.03	248.40	76.48	110.91	5.70	441.49	264.13	12.66	108.26	0.39	385.06	25.16	132	10.10
Whillan Beck	6.21	240.92	77.39	107.15	5.20	430.65	253.06	4.25	100.44	0.64	357.76	26.56	126	5.28
Hardknott Gill	6.18	162.94	45.61	199.41	2.91	410.86	203.71	5.40	114.40	0.25	323.51	30.39	164	1.02
Whelpside Ghyll	6.16	218.56	55.07	187.37	0.00	461.01	224.85	29.59	142.92	0.20	397.36	24.35	140	1.15
Wyth Burn	6.64	95.71	28.04	112.66	0.00	236.41	97.03	0.00	41.57	0.52	138.60	42.20	88	3.74
Launchy Ghyll	6.43	87.69	18.00	93.47	0.00	199.15	100.76	0.00	34.78	0.25	135.54	26.24	88	1.26
Shoulthwaite Gill	6.91	147.42	41.10	219.97	0.00	408.48	200.16	0.00	82.37	0.74	282.53	97.93	172	1.22
Coledale Beck	5.82	209.24	72.32	240.38	2.57	524.51	292.24	0.00	189.84	1.53	482.08	18.62	174	2.20
Liza Beck	5.29	144.54	48.27	20.05	3.45	216.31	137.56	6.15	57.33	0.49	201.04	-3.84	130	7.14
Mill Beck 2	6.16	132.45	48.70	120.24	0.00	301.40	162.94	0.00	94.71	0.76	257.65	22.45	148	2.05
Sour Milk Gill	5.68	115.88	28.50	57.68	0.00	202.06	121.25	4.09	40.42	0.49	165.77	11.49	96	2.23
Styhead Gill	5.86	87.97	27.31	141.81	2.46	259.55	151.51	12.53	56.09	0.26	220.12	21.90	104	6.17
Glenridding Beck	6.19	117.45	41.53	139.27	0.00	298.26	127.56	10.24	65.43	0.69	203.23	40.81	142	4.23
Glencoyne Beck	6.60	109.60	39.82	181.98	0.00	331.40	126.44	0.00	75.87	0.14	202.32	87.42	184	2.56
Aira Beck	6.47	106.51	36.07	122.15	0.00	264.74	117.52	0.00	45.98	0.29	163.49	51.73	214	7.28
Parkhouse Gill	6.94	81.77	51.27	178.19	2.05	313.28	54.98	4.49	28.84	0.88	88.31	200.86	294	0.96
Fusedale Beck	6.71	75.60	39.78	185.85	1.52	302.75	69.50	0.00	39.07	0.38	108.57	133.61	318	3.46
Heltondale Beck	6.85	80.12	57.46	149.82	2.45	289.85	113.52	0.00	55.05	0.73	168.57	81.51	352	1.22
Cawdale Beck	6.78	84.82	43.02	127.54	1.97	257.36	64.40	4.34	32.38	0.23	101.12	98.82	334	1.75
Gatescarth Beck	6.69	63.99	41.76	157.95	0.00	263.70	60.72	5.97	41.71	1.20	108.39	100.06	200	1.66
Naddle Beck	6.68	100.84	50.37	251.37	0.00	402.58	141.64	0.00	83.12	1.21	224.76	82.44	170	2.81
Mosedale Beck	6.59	84.36	62.56	170.04	0.00	316.97	132.14	0.00	58.97	0.34	191.11	61.92	174	4.88
Tailbert Gill	6.74	120.38	71.36	171.32	2.65	365.71	144.71	0.00	65.17	1.31	209.88	59.60	200	0.35

D.2 Flow-weighted chemistry

Table D6 – Flow-weighted ion chemistry, alkalinity, silica and pH data

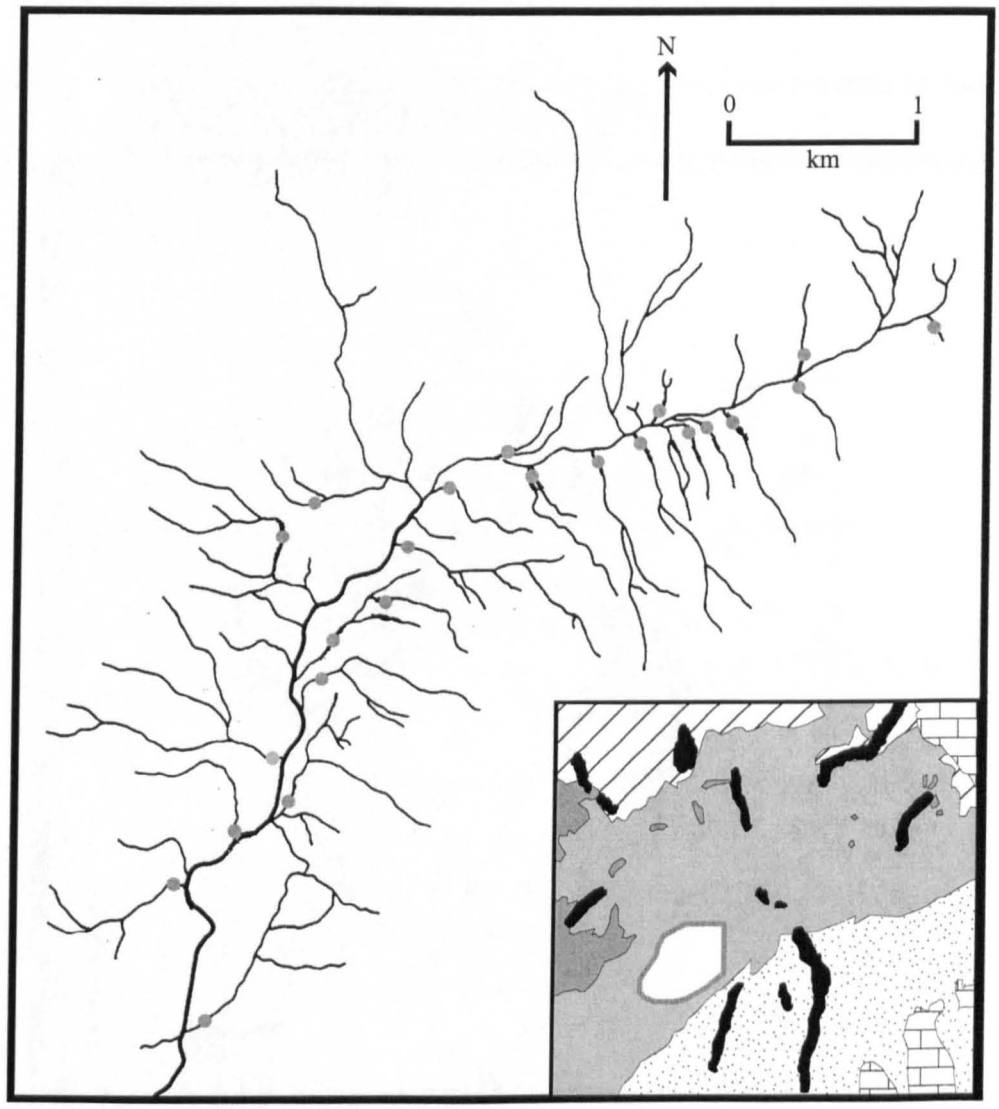
(Annual weighted means - Units are μeq l^{-1} for major ions and alkalinity, μg l^{-1} for silica, pH units for pH)

Sample	pH	Na	Mg	Ca	K	SBC	Cl	NO3	SO4	F	SAA	Alk	SiO2
Rydal Beck	6.79	96.55	52.73	142.14	1.38	292.80	116.41	12.08	81.04	0.74	209.53	84.60	162.89
Stock Ghyll	6.83	187.50	54.88	215.48	3.56	461.42	242.84	24.47	88.48	0.74	355.79	142.16	142.45
How Beck	7.09	95.89	56.05	230.16	5.32	387.43	105.63	28.39	86.14	0.89	220.15	213.43	188.26
Dale Park Beck	6.81	159.87	59.32	228.29	4.80	452.28	195.93	33.40	123.36	0.99	352.69	153.30	242.46
Low Cunsey Beck	7.07	158.57	69.93	332.86	6.54	567.91	216.64	33.88	129.86	1.27	380.38	240.41	231.11
Belle Grange Beck	7.00	138.06	51.08	213.82	5.24	408.20	156.06	8.35	128.70	1.58	293.12	130.65	205.55
Red Dell Beck	6.41	116.16	84.06	115.25	8.78	324.25	99.98	28.17	157.76	1.17	285.91	43.46	112.02
Torver Beck	7.03	97.11	56.94	163.35	4.37	321.77	107.52	16.83	89.91	0.79	214.26	115.84	139.04
Washfall Beck	7.05	113.42	56.46	176.43	4.16	350.48	96.35	4.15	66.69	1.20	167.19	151.24	155.03
Mill Beck 1	7.18	239.05	137.27	655.66	28.51	1060.49	349.37	238.66	176.07	0.96	764.10	429.73	159.90
Stony Beck	6.74	107.14	55.82	114.02	2.11	279.10	84.01	5.19	77.20	1.07	166.40	84.41	80.91
Hagg Gill	6.91	90.49	46.69	197.13	3.12	337.43	106.00	16.92	89.73	0.88	212.65	137.83	164.39
Trout Beck	6.80	80.82	32.20	126.20	2.02	241.23	75.37	9.21	50.58	1.31	135.16	76.04	115.14
Woundale Beck	6.83	98.62	42.70	106.70	2.14	250.16	96.43	3.55	41.06	0.91	141.05	82.49	101.07
Hall Gill	7.01	190.71	110.24	211.54	2.06	514.55	87.18	7.85	82.80	1.60	177.83	147.25	131.84
Chapel Beck	7.27	128.51	109.03	415.82	12.87	666.23	157.57	85.26	87.66	1.37	330.49	451.35	248.85
Chapel Beck Trib	7.30	108.66	63.04	334.32	6.46	512.49	88.34	48.34	71.33	1.10	208.01	294.95	223.77
Grayrigg Hall Beck	7.27	122.99	86.48	261.90	12.86	484.22	142.15	34.60	66.26	1.39	243.00	249.57	226.63
Flodder Beck	7.09	76.49	52.36	221.62	7.62	358.08	65.03	35.47	28.61	1.50	129.10	220.82	225.02
St Sundays Beck	7.08	158.34	76.55	305.67	8.07	548.63	141.53	33.21	67.78	1.42	242.52	281.28	224.68
Killington Res Trib	6.90	119.67	84.39	229.13	5.47	438.65	171.57	28.12	104.59	1.27	304.28	147.90	252.93
River Mint Trib	7.02	114.39	83.63	218.21	5.19	421.42	144.58	10.17	103.01	1.12	257.76	161.96	202.80
Borrow Beck	6.71	128.77	63.26	183.75	5.20	380.98	148.42	0.26	95.65	0.76	244.33	124.33	113.43
Bannisdale Beck	6.92	145.68	87.22	176.66	3.78	413.34	87.68	2.33	83.74	0.84	173.75	131.57	134.55
River Sprint	6.95	69.98	41.13	210.21	3.33	324.66	85.92	18.19	74.98	0.65	179.09	208.69	174.81
Moasdale Beck	5.53	108.18	30.58	34.35	3.92	177.03	95.13	13.21	53.72	0.66	162.06	1.10	148.07
Castle How Beck	6.18	180.69	63.17	104.20	3.51	351.57	189.28	33.12	100.66	1.26	323.07	15.84	199.73
Tarn Beck	6.51	113.18	49.01	80.62	3.54	246.34	111.71	22.59	66.96	0.84	201.26	34.59	119.26
Sling Beck	6.42	97.87	40.31	56.06	0.51	194.74	96.72	0.22	43.81	0.82	140.74	45.72	118.60
Holehouse Gill	6.97	114.15	69.29	122.99	4.11	310.53	120.83	0.00	48.11	0.93	168.94	153.15	315.29
Crosby Gill	7.01	114.97	52.50	126.29	4.09	297.85	112.50	6.31	48.50	0.84	167.31	125.40	184.49
Greendale Gill	6.51	196.11	87.15	82.97	5.14	371.36	216.77	13.56	89.50	0.98	319.83	44.61	186.79
Nether Beck	6.40	175.94	62.48	90.73	5.22	334.37	189.10	12.13	85.93	0.84	287.17	30.80	118.66
Whillan Beck	6.45	167.44	65.03	88.52	5.22	326.23	183.64	7.57	78.63	0.99	269.84	38.92	124.30
Hardknott Gill	6.59	121.84	45.61	158.92	3.94	330.31	149.32	10.37	98.68	1.12	258.37	79.88	151.86
Whelpside Ghyll	6.59	163.53	49.02	155.56	1.50	369.60	171.19	27.47	118.98	0.91	317.64	35.98	116.37
Wyth Burn	6.67	81.55	28.37	106.64	0.68	217.24	81.51	3.84	44.03	0.72	129.38	57.50	75.16
Launchy Ghyll	6.70	81.65	22.06	103.80	1.09	208.60	92.77	1.14	41.82	0.49	135.74	63.43	73.06
Shoulthwaite Gill	6.99	119.34	42.39	201.61	1.53	364.87	160.38	3.34	79.50	0.95	243.22	128.37	146.94
Coledale Beck	6.47	157.24	75.90	199.33	5.05	437.52	222.53	1.64	169.60	1.51	393.77	71.11	140.97
Liza Beck	5.61	129.41	50.90	23.48	3.92	207.70	129.14	6.36	54.64	0.82	190.15	4.28	119.08
Mill Beck 2	6.31	111.83	50.80	109.75	1.63	274.01	142.86	0.00	86.11	1.11	228.97	45.36	120.58
Sour Milk Gill	6.01	109.15	32.18	66.39	1.00	208.72	111.14	9.80	50.90	0.49	171.84	17.40	84.98
Styhead Gill	6.28	71.53	28.83	119.80	2.73	222.89	113.00	21.72	57.40	0.52	192.12	56.21	94.02
Glenridding Beck	6.62	96.74	43.76	137.97	1.26	279.73	107.25	11.87	66.24	0.94	185.37	81.89	124.53
Glencoyne Beck	6.95	91.13	44.29	183.92	1.72	321.06	112.71	3.95	80.33	0.54	196.99	142.27	156.14
Aira Beck	6.76	103.09	41.88	133.75	0.75	279.47	119.92	0.00	55.12	0.48	175.04	97.88	187.60
Parkhouse Gill	7.20	109.12	94.09	280.95	5.56	489.72	77.87	7.51	57.41	1.39	142.80	368.45	252.44
Fusedale Beck	7.07	70.65	48.77	199.93	2.67	322.02	71.51	0.00	47.61	0.66	119.11	224.25	268.64
Heltondale Beck	7.25	87.74	81.01	199.20	4.61	372.56	70.76	0.00	29.47	0.83	100.23	229.91	322.75
Cawdale Beck	7.09	83.84	57.36	154.30	3.83	299.32	76.71	1.84	40.61	0.40	119.16	189.40	320.08
Gatescarth Beck	6.94	64.98	55.21	188.43	1.39	310.00	70.58	9.32	55.13	0.77	135.03	187.70	170.84
Naddle Beck	6.93	88.33	57.07	250.93	1.44	397.77	117.08	3.54	88.72	1.20	209.33	217.36	146.09
Mosedale Beck	6.91	69.16	64.02	163.97	1.30	298.45	85.74	0.70	51.50	0.54	137.94	189.32	140.52
Tailbert Gill	6.89	154.77	132.57	291.52	7.24	586.11	90.56	0.69	53.64	1.05	144.89	301.80	178.25

D.3 Description of the historical studies used[#]

1. Sutcliffe & Carrick (1973a,b) sampled twenty-three small becks draining the Borrowdale Volcanic geological group on a weekly basis between July and November 1972. These streams are located in the upper Duddon basin (Figure D1).

Figure D1 - Location of the 23 becks draining the Upper Duddon basin as reported by Sutcliffe and Carrick (1973a,b). (Sites in blue are same as sites in the present study)



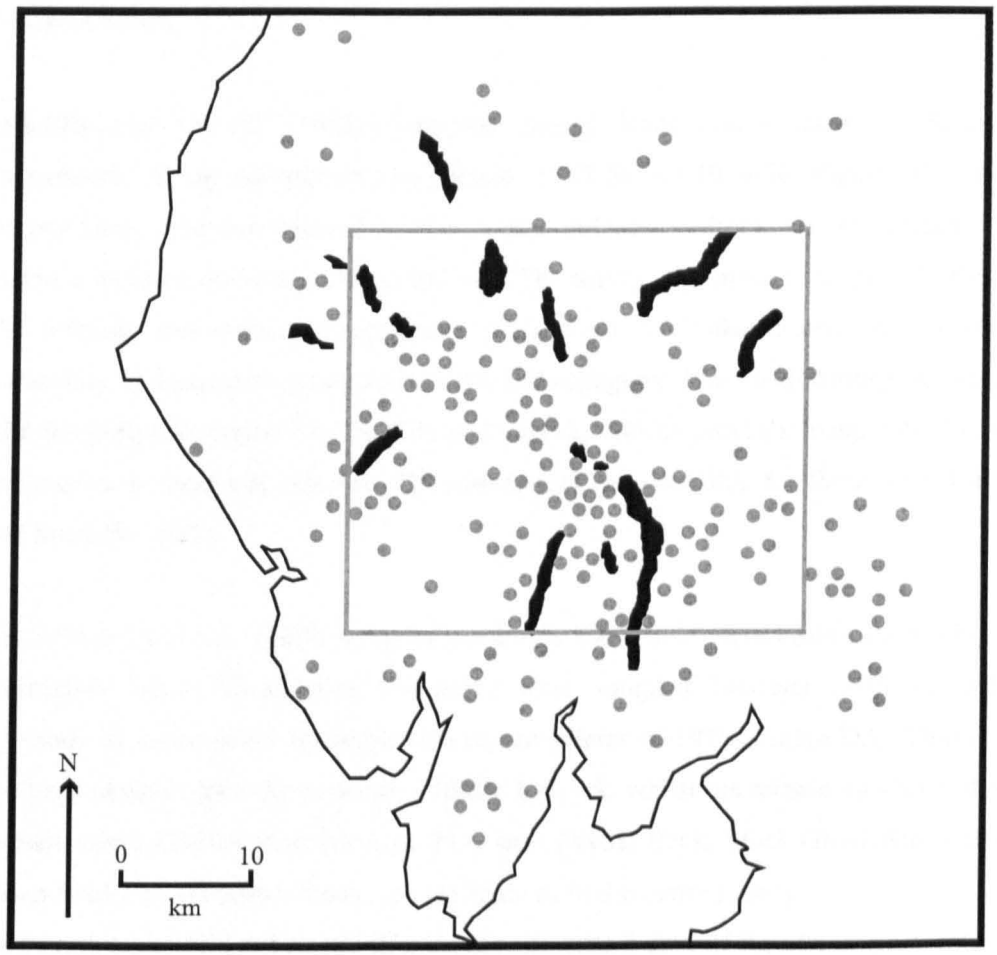
The survey was initiated to provide a detailed picture of the water chemistry in the Duddon Valley with respect to the major ions thought to affect the distribution of benthic stream invertebrates. One site (Castle How Beck) is the same as in the current study. The published literature (i.e. Sutcliffe and Carrick, 1973a,b) provides data about

[#] **GLOSSARY:** Some local terminology is used by the historical studies – A beck is the local term in Northern England for a rapidly flowing stream and a tarn is the local term in Northern England (especially the Lake District) for a small lake.

the distribution of macroinvertebrate taxa, and the mean and range of pH, calcium, magnesium, potassium, sodium and chloride concentrations for each stream. The raw data is also available for these ions (Carrick and Sutcliffe, 1983).

2. Sutcliffe et al., (1982) sampled twenty-four lakes and tarns on a weekly basis between April 1974 and March 1978 (Figure D2). Of the twenty-four sites, nine were located on Borrowdale Volcanic bedrock, eight on Silurian Slate bedrock and seven on Skiddaw Slate bedrock.

Figure D2 - Location of 154 lakes and tarns in the Lake District as reported by Sutcliffe et al. (1982), and, Sutcliffe and Carrick (1983a)



The survey was initiated to provide data on the chemical composition of precipitation and lakes and tarns in the Lake District to assess the long-term and seasonal variability in water chemistry. The published literature (i.e. Sutcliffe *et al.*, 1982) provides mean data for pH, calcium, magnesium, potassium, sodium, chloride, sulphate, nitrate and alkalinity for each lake / tarn. The raw data is also available for these ions (Carrick and Sutcliffe, 1982).

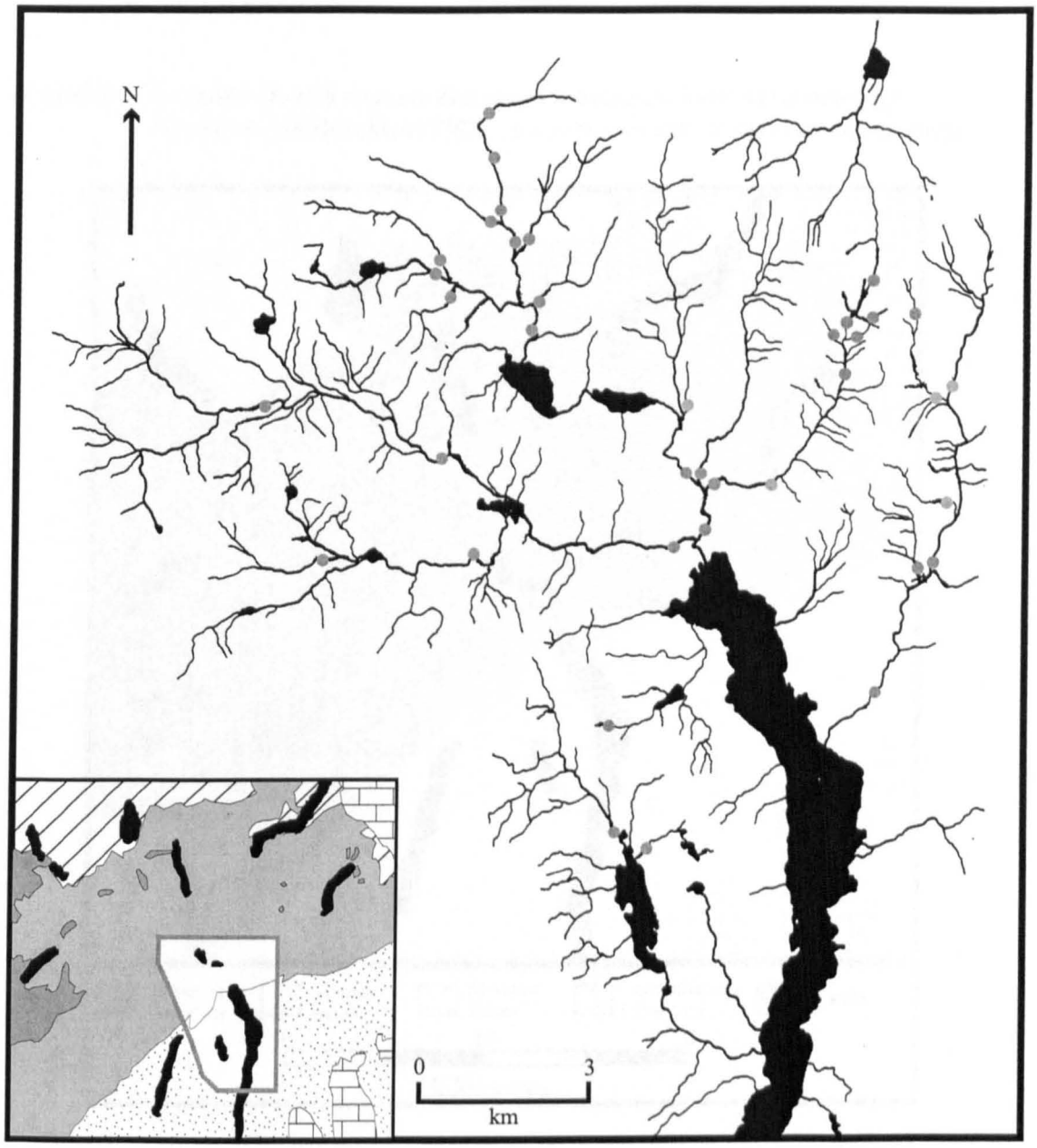
3. Sutcliffe and Carrick (1983a) infrequently sampled one hundred and thirty tarns between 1953 and 1975 (Figure D2). Of these tarns, sixty-three were located on Borrowdale Volcanic bedrock, fifty-one on Silurian Slate bedrock, nine on Skiddaw Slate bedrock and seven on Carboniferous bedrock. The survey was initiated to provide chemical composition data for tarns in the Lake District in relation to geological variables. The published literature (i.e. Sutcliffe and Carrick, 1983a) provides geometric mean data and 95% confidence limits for the whole period of a number of elements (i.e. calcium, magnesium, potassium, sodium, chloride, sulphate, nitrate and alkalinity) on the basis of geological group. The raw data is also available for these ions (Carrick and Sutcliffe, 1982).

4. Sutcliffe and Carrick (1983a) sampled twenty lakes (same lakes as Study 2) infrequently during summer for two periods, 1955-56 and 1974-76 (Figure D2). Of the twenty lakes, nine were located on Borrowdale Volcanic bedrock, six on Skiddaw Slate bedrock and five on Silurian Slate bedrock. The survey was initiated to provide data on the chloride and sodium composition of lakes in the Lake District to assess the variability in long-term precipitation and anthropogenic (i.e. road-salting) influences. The published literature (i.e. Sutcliffe and Carrick, 1983a) provides mean data for both periods for sodium and chloride. The raw data is also available for these ions (Carrick and Sutcliffe, 1982).

5. Sutcliffe and Carrick (1983b) sampled streams in the Windermere basin on a weekly-to-fortnightly basis. Thirty-eight tributaries were sampled between 1975-76, and a substudy of seven of the tributaries during the winter of 1976 (Figure D3). Thirty-two (or four) streams drain Borrowdale volcanic bedrock, whilst the remaining six (or three) streams drain Silurian Slate bedrock. Five sites (Rydal Beck, Stock Ghyll, Stony Beck, Trout Beck and Woundale Beck) are the same as in the current study.

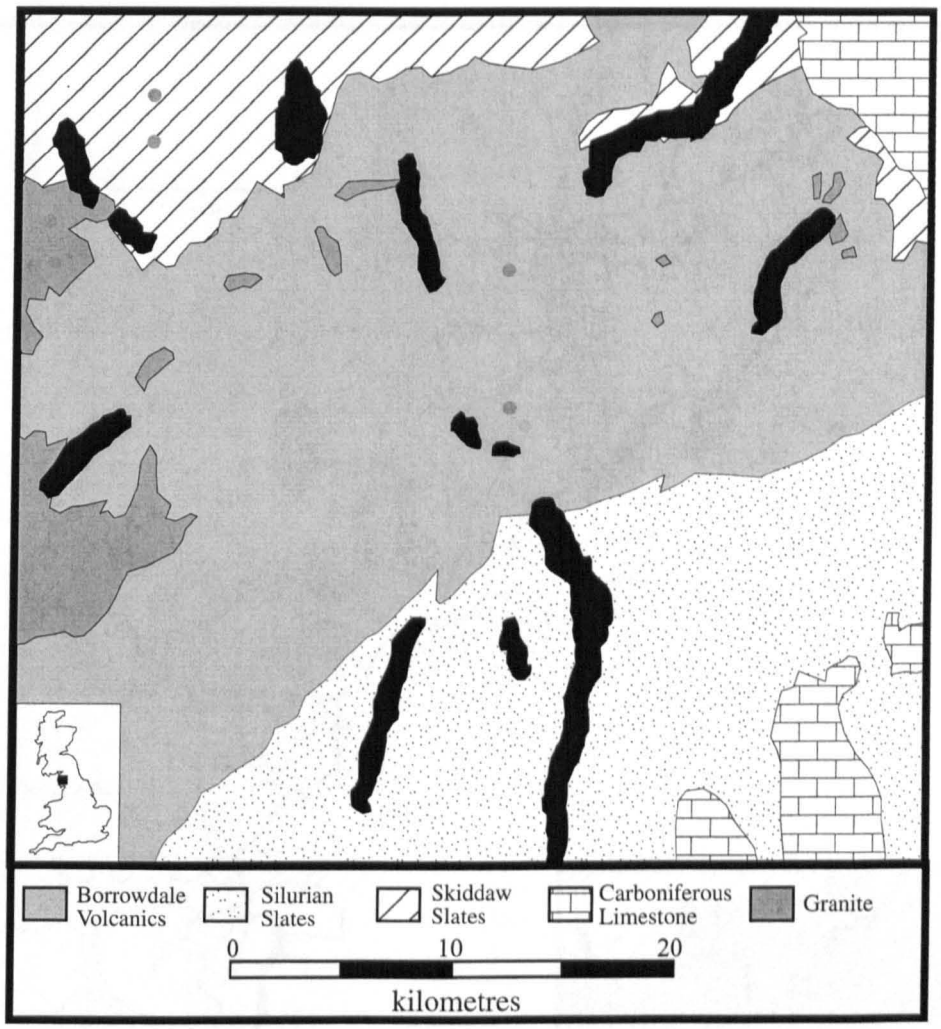
   The survey was initiated to provide baseline chemical data of the streams draining the Windermere basin to assess the long-term and seasonal variability in chemical compositions. The published literature (i.e. Sutcliffe and Carrick, 1983b) provides mean data and ranges for calcium, magnesium, potassium, sodium and chloride in each stream. The raw data is also available for these ions (Carrick and Sutcliffe, 1983).

Figure D3 - Location of the 38 streams draining the Windermere basin as reported by Sutcliffe and Carrick (1983b). (Sites in blue are same as sites in the present study)



6. Adamson & Benefield (1987) sampled eight streams on a monthly basis between June 1980 and September 1981 (Figure D4). Three streams drain Borrowdale volcanic bedrock, three streams drain Granite bedrock and the remaining two streams drain Skiddaw Slate bedrock.

Figure D4 - Location of the 8 streams draining 3 lithological units as reported by Adamson and Benefield (1987). (Site in blue are same as site in the present study)



The survey was initiated to assess the chemical data of the streams in relation to geological variables. The published literature (i.e. Adamson and Benefield, 1987) provides mean data for the whole study of calcium, magnesium, potassium, sodium and chloride for each stream. The raw data is available from the author upon request.

7. Prigg (1983) sampled twenty-nine streams draining Borrowdale Volcanic bedrock and twenty-four streams draining granite bedrock four times between January and August 1982. These streams are located in the Duddon (Figure D5) and Esk (Figure D6) basins.

Figure D5 - Location of the 29 streams draining the Duddon basin as reported by Prigg (1983)
(Sites in blue are same as sites in the present study)

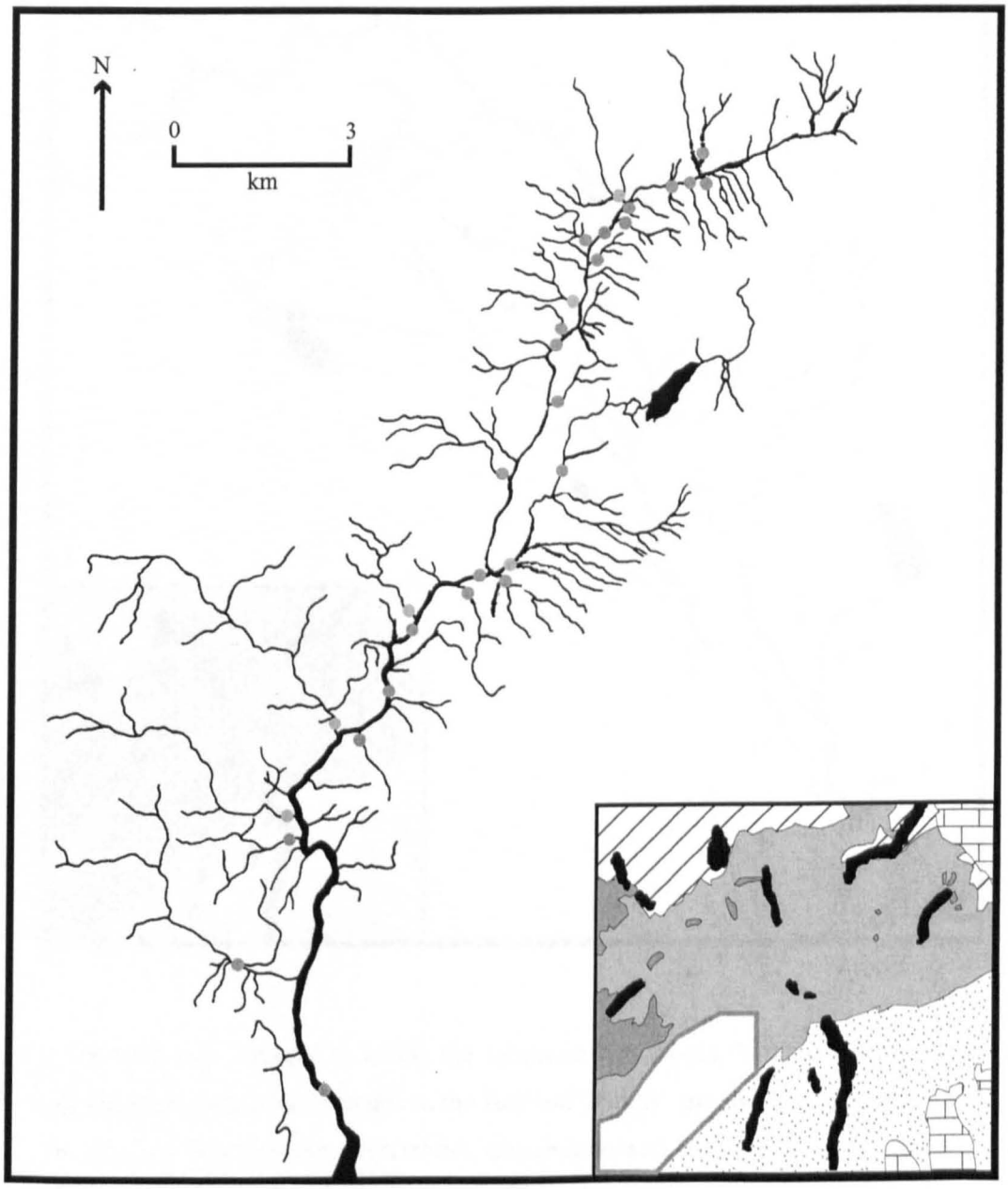
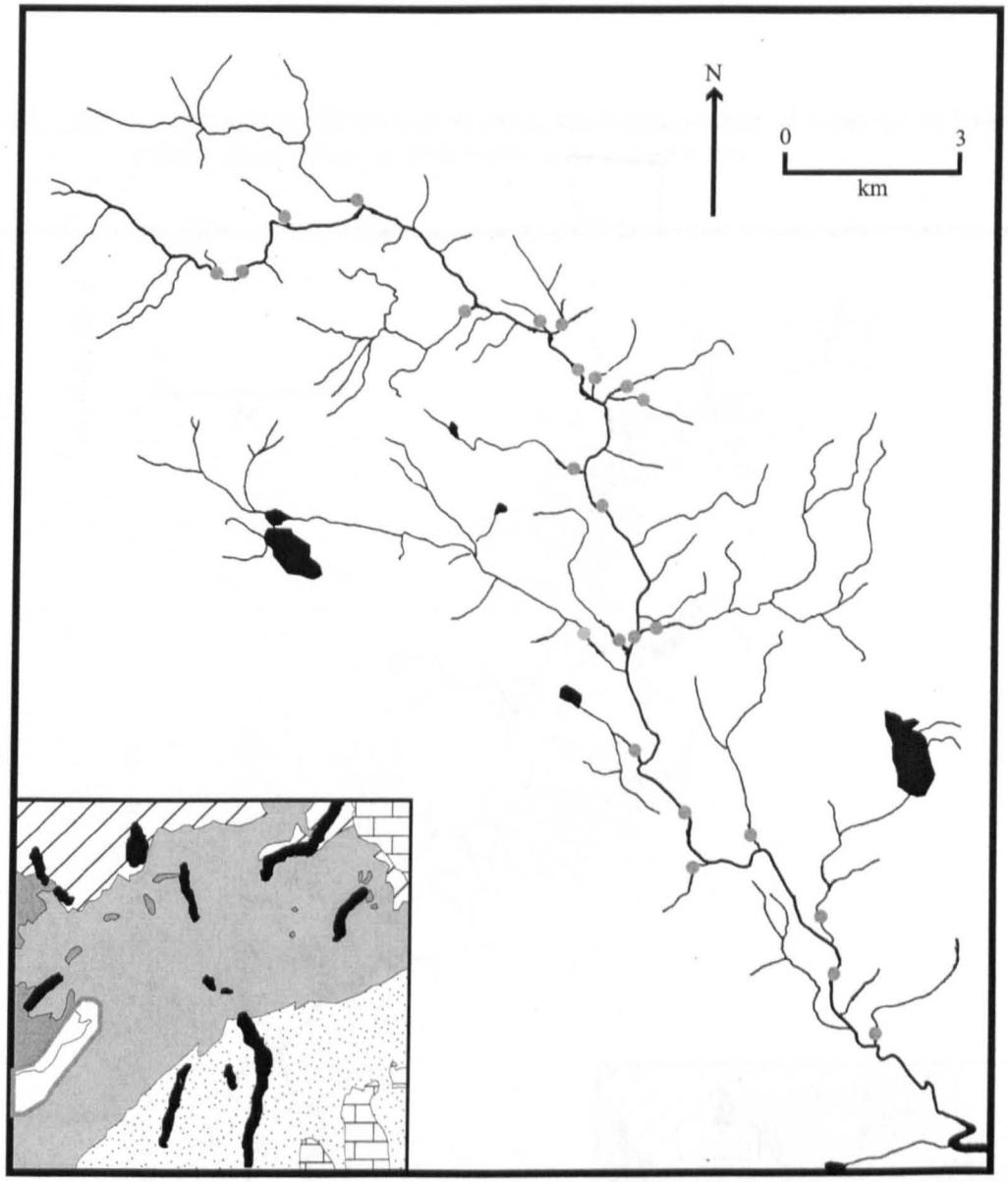


Figure D6 - Location of the 24 streams draining the Esk basin as reported by Prigg (1983)
(Sites in blue are same as sites in the present study)



The survey was initiated to assess the salmonid fish stocks, benthic macroinvertebrate and chemical data of the streams in the Esk and Duddon basins. The published literature (i.e. Prigg, 1983) provides invertebrate distribution and fish densities, as well as mean data and ranges of pH, alkalinity and calcium for each stream. Seven sites (Moasdale Beck, Castle How Beck, Tarn Beck, Sling Beck, Holehouse Gill, Crosby Gill and Whillan Beck) are the same as in the current study.

8. Crawshaw (1984) sampled thirty-eight streams on a quarterly basis between January 1982 and December 1983. Twenty-two streams drain Borrowdale Volcanic bedrock in the Duddon basin (Figure D7) and the remaining sixteen streams drain granite bedrock in the Esk basin (Figure D8).

Figure D7 - Location of the 22 streams draining the Duddon basin as reported by Crawshaw (1984). (Sites in blue are same as sites in the present study)

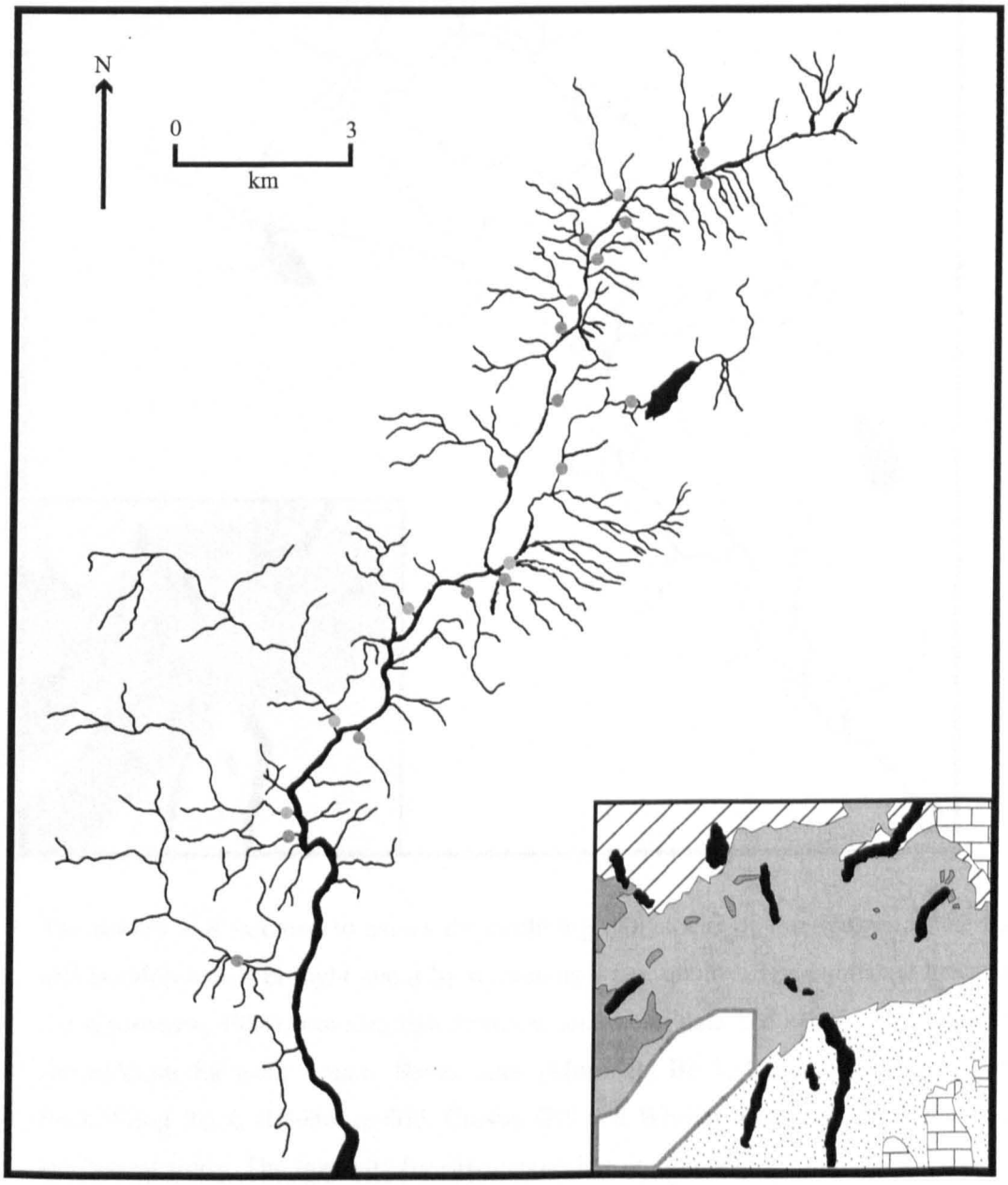
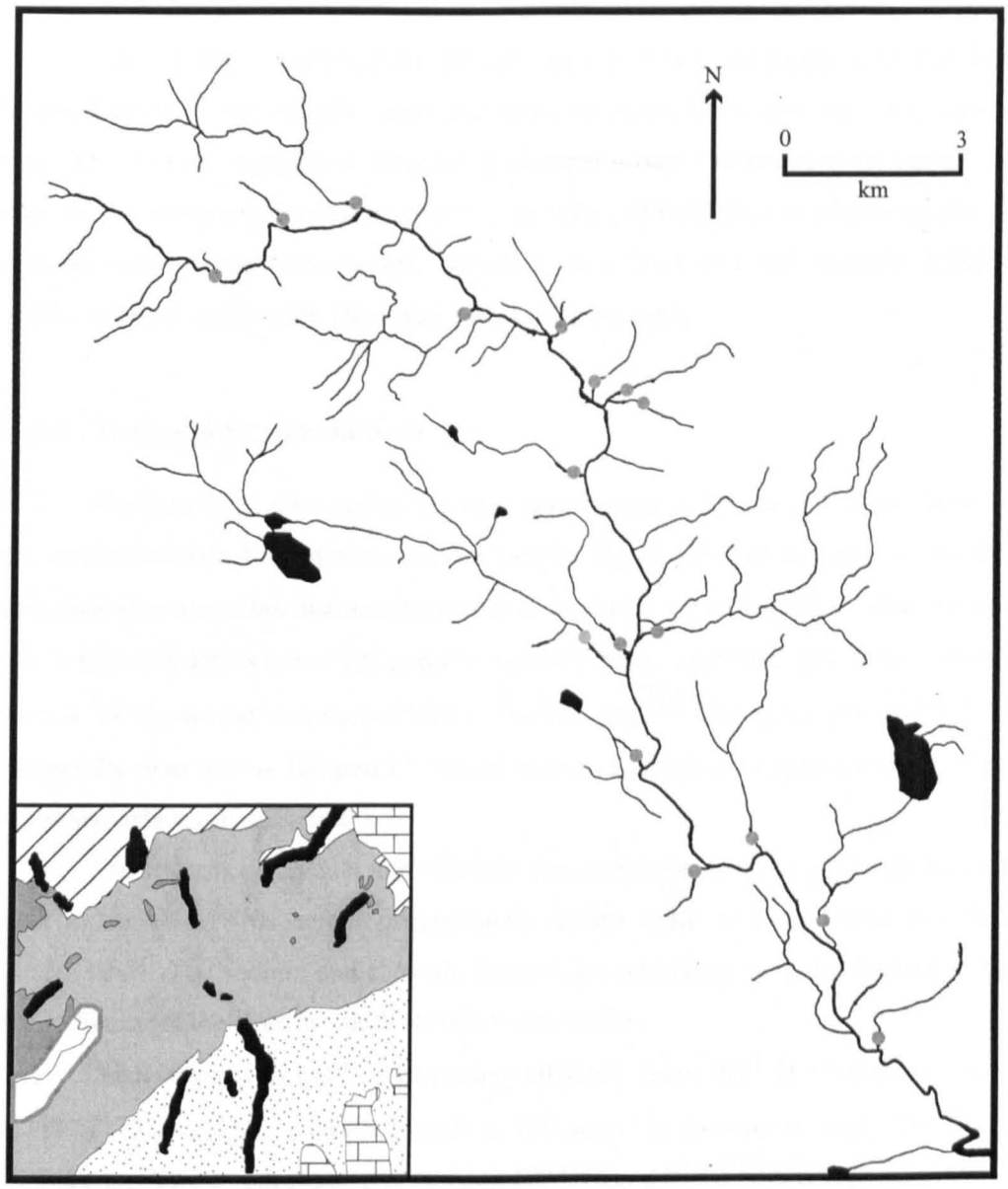


Figure D8 - Location of the 16 streams draining the Esk basin as reported by Crawshaw(1984).
(Sites in blue are same as sites in the present study)



The survey was initiated to assess the declining fish stocks of the streams in the Esk and Duddon basins brought about by worsening water quality. The published literature (i.e. Crawshaw, 1984) provides fish densities and mean data and ranges of aluminium and calcium for each stream. Seven sites (Moasdale Beck, Castle How Beck, Tarn Beck, Sling Beck, Holehouse Gill, Crosby Gill and Whillan Beck) are the same as in the current study. The raw data for pH, magnesium, nitrate and alkalinity are available from North-West Water upon request.

D.4 Comparison of current and historical data

The current concentrations of the streams were compared with the historical concentrations of the streams, lakes and tarns to assess the water chemistry trends over time. The data are segregated using the geological groups but because the stream and tarn data are not really comparable and each study uses different streams / lakes means that this method is not scientifically robust. However, as a 'look and see' exercise it provides a useful measure of the water chemistry variability over time.

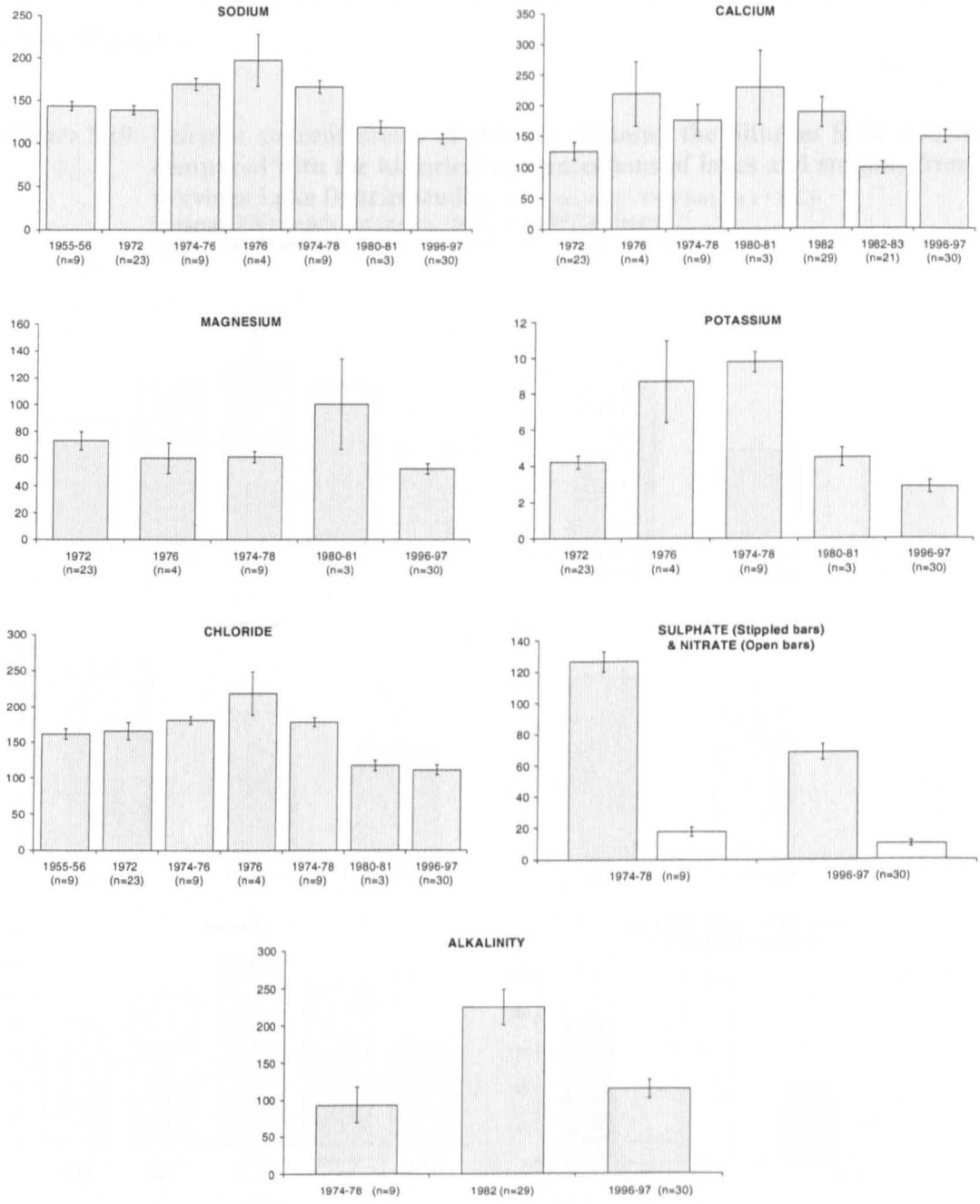
D.4.1 Tarn and Stream data (1)

The data from nine studies for sites draining (or in the case of lakes / tarns located on) the Borrowdale Volcanics were examined by Figure D9. Calcium concentrations seem to exhibit periods of decline and growth over time (i.e. very dynamic). Concentrations are low in the early 1970s (circa 125 $\mu eq\ l^{-1}$), but then seem to increase to a maximum in during the late 1970s and the very early 1980s (circa 225 $\mu eq\ l^{-1}$). During the period 1982-83, they fall rapidly to as low as 100 $\mu eq\ l^{-1}$, before recovering slightly to approximately 150 $\mu eq\ l^{-1}$ in the late 1990s (i.e. this study).

The sodium, potassium and chloride concentrations seem to gradually increase to a peak in the mid-1970s before progressively falling again to their lowest values in the current study. The sodium and chloride patterns are reflecting the perturbations in the sea-salt influence of the Borrowdale Volcanic water bodies.

Other patterns include, (i) Increasing alkalinity from 1974-76 (100 $\mu eq\ l^{-1}$) to a peak in 1982 (225 $\mu eq\ l^{-1}$) before falling again to 100 $\mu eq\ l^{-1}$ in the current study; and (ii) Falling sulphate and nitrate concentrations between 1974-76 and the current study.

Figure D9 - Current concentrations of streams draining the Borrowdale Volcanic bedrock compared with the historical concentrations of lakes and streams from 6 previous Lake District studies (Units are μeq l^{-1}. Error bars are ± 1 S.E.)
Streams: **1972** *(Sutcliffe and Carrick, 1973a,b);* **1976** *(Sutcliffe and Carrick, 1983b);* **1980-81** *(Adamson and Benefield, 1987);* **1982** *(Prigg, 1983);* **1983** *(Crawshaw, 1984);* **1996-97** *(This study).*
Lakes: **1955-56 and 1974-76** *(Sutcliffe and Carrick, 1983a);* **1974-78** *(Sutcliffe et al., 1982).*

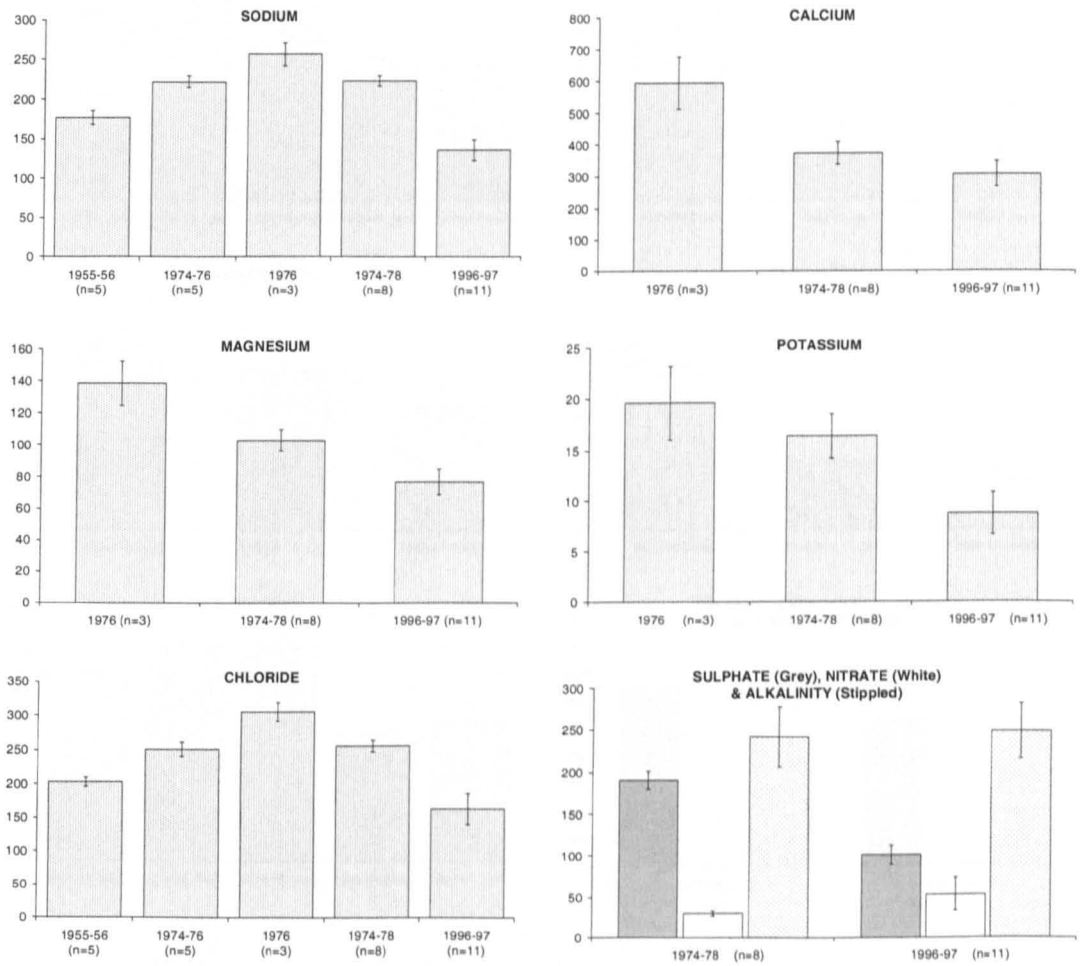


The ion concentrations from sites draining the Silurian Slates were examined by Figure D10. Again sodium and chloride concentrations seem to gradually increase to a peak in the mid-1970s before progressively falling again to their lowest values in the current study, thus reflecting the perturbations in the sea-salt influence of the Silurian Slate water

bodies.

Other patterns include, the gradual decline of calcium, magnesium and potassium concentrations between 1976 and the present study (600 to 300 μeq l^{-1}, 140 to 80 μeq l^{-1}, and 20 to 10 μeq l^{-1} respectively); a decline in sulphate between 1974-78 and the current study (200 to 100 μeq l^{-1}); and an increase in nitrate between 1974-78 and the current study (30 to 50 μeq l^{-1}).

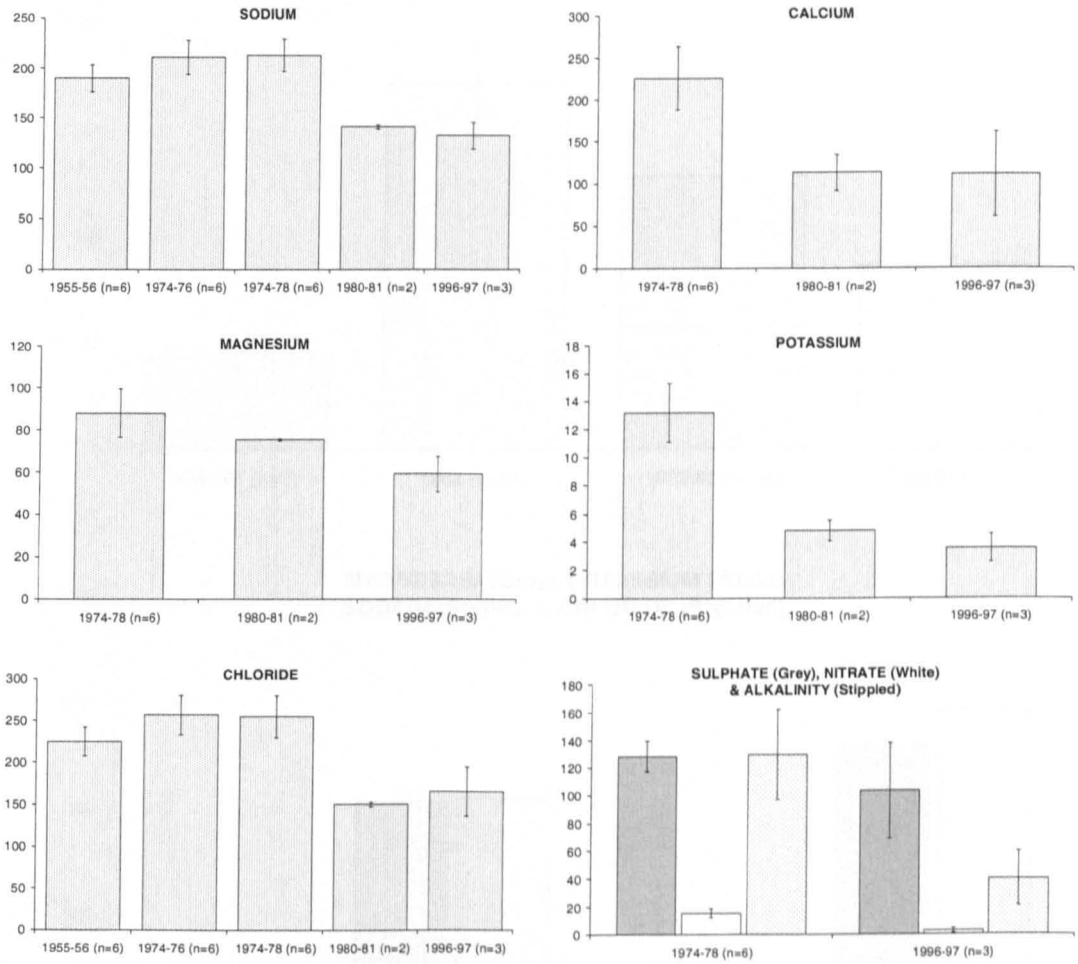
Figure D10 - Current concentrations of streams draining the Silurian Slate bedrock compared with the historical concentrations of lakes and streams from 4 previous Lake District studies. (Units are μeq l^{-1}. Error bars are ± 1 S.E.)
Streams: 1976 *(Sutcliffe and Carrick, 1983b);* **1996-97** *(This study).*
Lakes: 1955-56 and 1974-76 *(Sutcliffe and Carrick, 1983a);* **1974-78** *(Sutcliffe et al., 1982).*



The ion concentrations from sites draining the Skiddaw Slates were examined by Figure D11. Sodium and chloride concentrations seem to gradually increase to a peak in the mid-1970s before progressively falling again to their lowest values in the current study, thus reflecting the perturbations in the sea-salt influence of the Silurian Slate water bodies.

Other patterns include, the gradual decline of calcium, magnesium and potassium concentrations between 1974-76 and the present study (225 to 100 μeq l^{-1}, 90 to 60 μeq l^{-1}, and 13 to 4 μeq l^{-1} respectively); and of sulphate, nitrate and alkalinity between 1974-78 and the current study (200 to 100 μeq l^{-1}, 20 to 5 μeq l^{-1}, and 130 to 40 μeq l^{-1} respectively).

Figure D11 - Current concentrations of streams draining the Skiddaw Slate bedrock compared with the historical concentrations of lakes and streams from 4 previous Lake District studies. (Units are μeq l^{-1}. Error bars are ± 1 S.E.)
Streams: 1980-81 *(Adamson and Benefield, 1987);* **1996-97** *(This study).*
Lakes: 1955-56 and 1974-76 *(Sutcliffe and Carrick, 1983a);* **1974-78** *(Sutcliffe et al., 1982).*

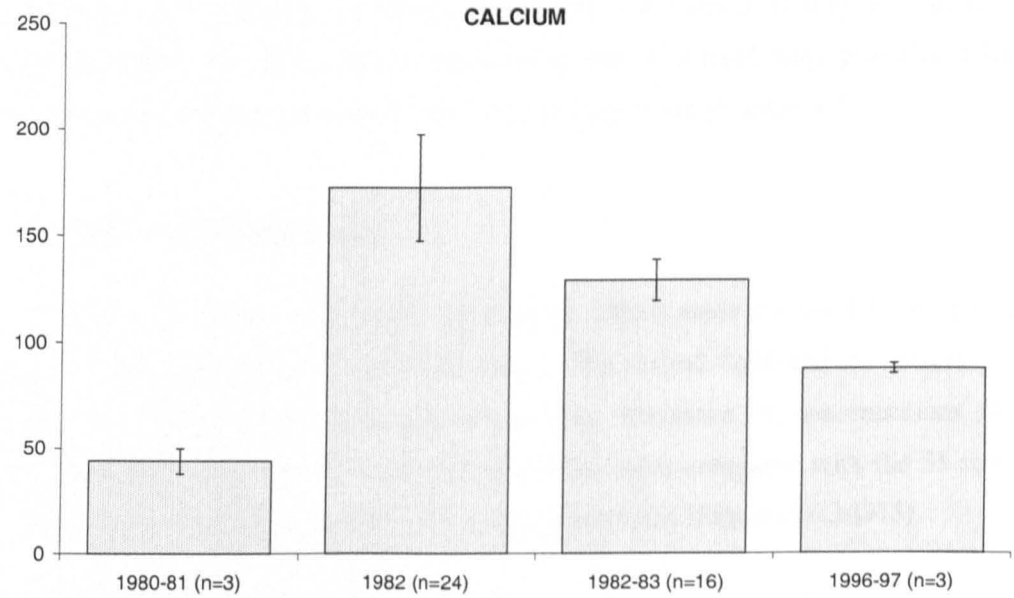


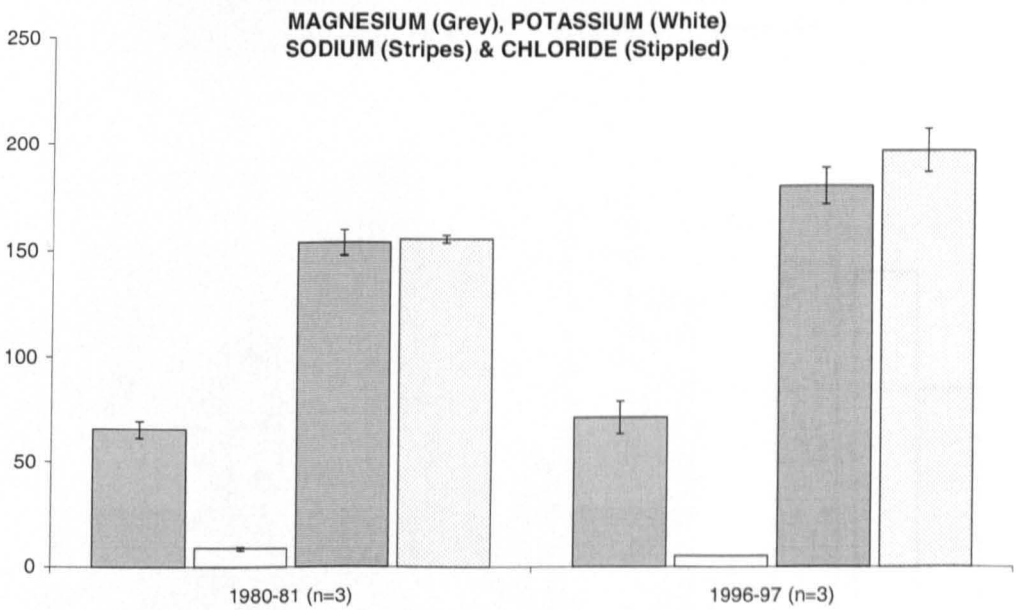
The ion concentrations from sites draining Granite bedrock were examined by Figure D12. Calcium concentrations are lowest in 1980-81 (<50 μeq l^{-1}), before increasing in 1982 (175 μeq l^{-1}), before declining again in 1982-83 (125 μeq l^{-1}) and the present study (100 μeq l^{-1}).

Other patterns include, the gradual increase of sodium and chloride concentrations

between 1980-81 and the present study (150 to 175 μeq l^{-1}, and 150 to 200 μeq l^{-1} respectively); and magnesium and potassium concentrations stay the same between 1980-81 and the current study (70 μeq l^{-1}, and 10 μeq l^{-1} respectively).

Figure D12 - Current concentrations of streams draining the Granite bedrock compared with the historical concentrations of streams from 4 previous Lake District studies. (Units are μeq l^{-1}. Error bars are ± 1 S.E.)
KEY: 1980-81 *(Adamson and Benefield, 1987);* **1982** *(Prigg, 1983);* **1983** *(Crawshaw, 1984);* **1996-97** *(This study).*





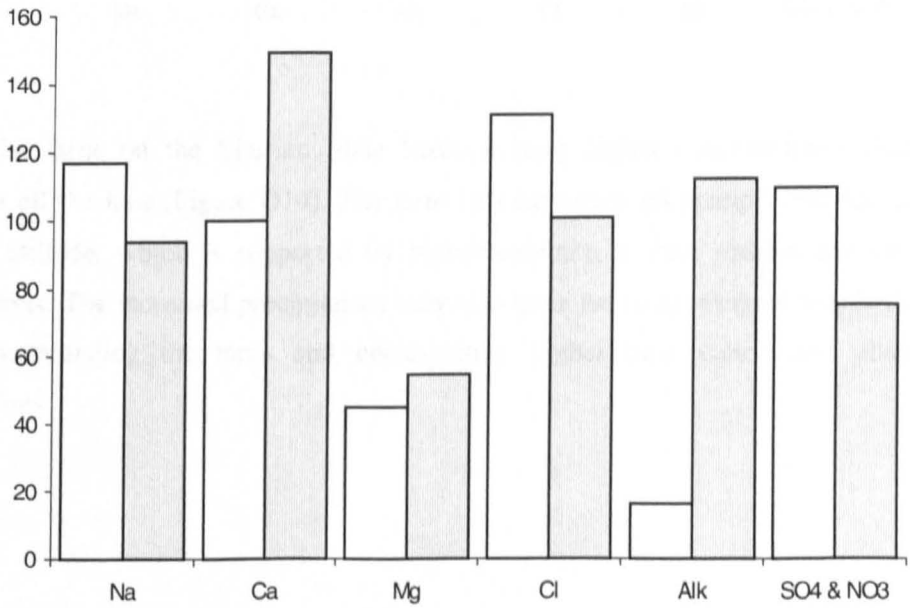
Summary

In general, the current study seems to record the lowest concentrations for the majority of ions in Borrowdale Volcanic, Silurian Slate and Skiddaw Slate water bodies. Present day Borrowdale Volcanic concentrations aren't dissimilar to those found in the early 1970s (Sutcliffe and Carrick, 1973a,b). This suggests that the mean concentrations of these water bodies haven't altered over the last 25 years. However, the intervening period displayed an improvement until the late 1970s followed by a decline until present day. Having said this, using mean data from a range of sites has inherent problems – the low and high concentrations (i.e. extremes) are disproportionately represented as they are 'pulled in' towards the mean. Therefore, the examination of the individual sites provides a better indication of water chemistry decline / improvement over time (Section 4.4).

D.4.2 Tarn vs Stream data (2)

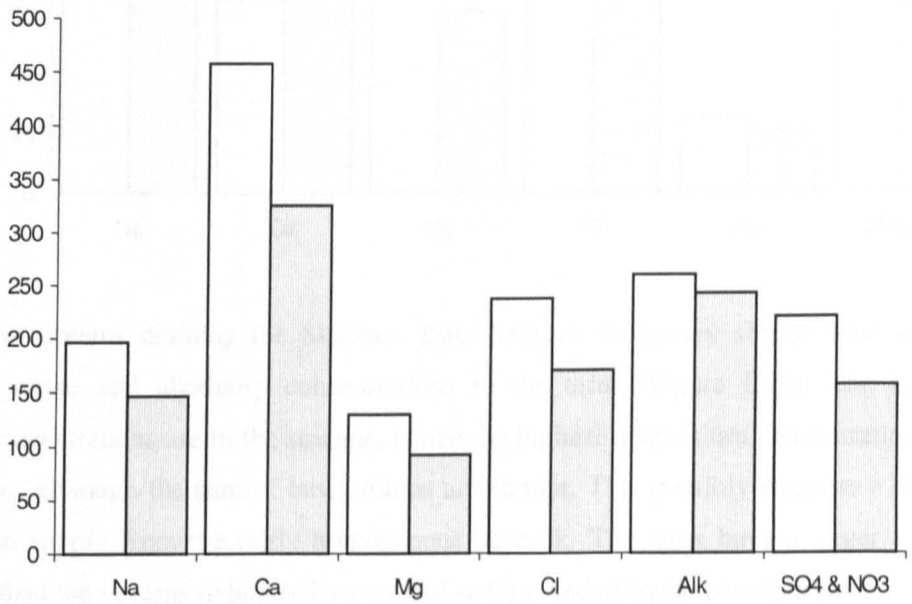
The tarns in Study 3 (Sutcliffe and Carrick, 1983a) were not used in the previous exercise because they cover a 20 year time period. The second 'look and see' exercise uses these tarns in relation to the current streamwater data. The mean ion concentrations of one hundred and thirty tarns (Sutcliffe and Carrick, 1983a) were compared with the 55 streams from the current study on the basis of their geological groups (Figures D13-D15).

Figure D13- Mean ion concentrations of 63 tarns sampled by Sutcliffe & Carrick, 1983a (open bars) and 30 streams from the current study (stippled bars) on the Borrowdale Volcanic geological group. (Units are $\mu eq\ l^{-1}$)



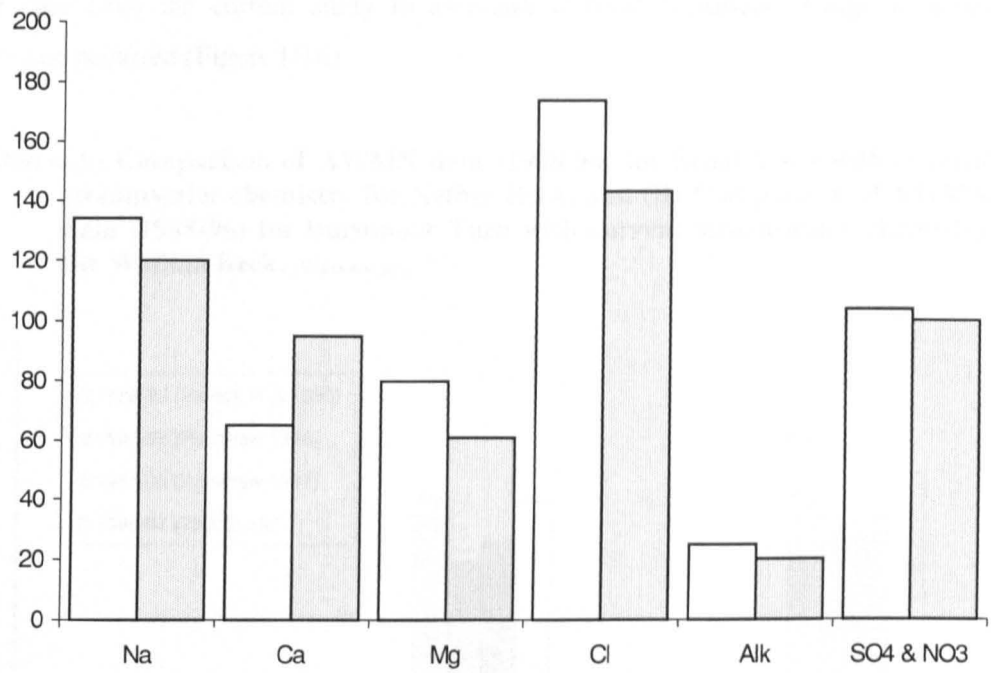
The streams draining the Borrowdale Volcanic bedrock have higher base cation and alkalinity concentrations than the tarns (Figure D13). The elevated concentrations may be due to an increase in weathering in the catchment because the streams are actively moving over, and eroding, the bedrock more than the "static" tarns, and soils tend to be thicker at lower altitudes thus enhancing base cation supply. In addition, the tarns receive increased acid precipitation due to higher altitudes, which is supported by higher sulphate, nitrate, sodium and chloride concentrations in the tarns.

Figure D14 - Mean ion concentrations of 51 tarns sampled by Sutcliffe & Carrick, 1983a (open bars) and 11 streams from the current study (stippled bars) on the Silurian Slates geological group. (Units are $\mu eq\ l^{-1}$)



The tarns on the Silurian Slate bedrock have higher concentrations than the streams for all the ions (Figure D14). The tarns receive increased precipitation because of their high altitude, which is supported by higher sulphate, nitrate, sodium and chloride concentrations. The increased precipitation may also have led to accelerated weathering of the area surrounding the tarns and consequently higher base cation and alkalinity concentrations.

Figure D15 - Mean ion concentrations of 9 tarns sampled by Sutcliffe & Carrick, 1983a (open bars) and 3 streams from the current study (stippled bars) on the Skiddaw Slates geological group. (Units are $\mu eq\ l^{-1}$)



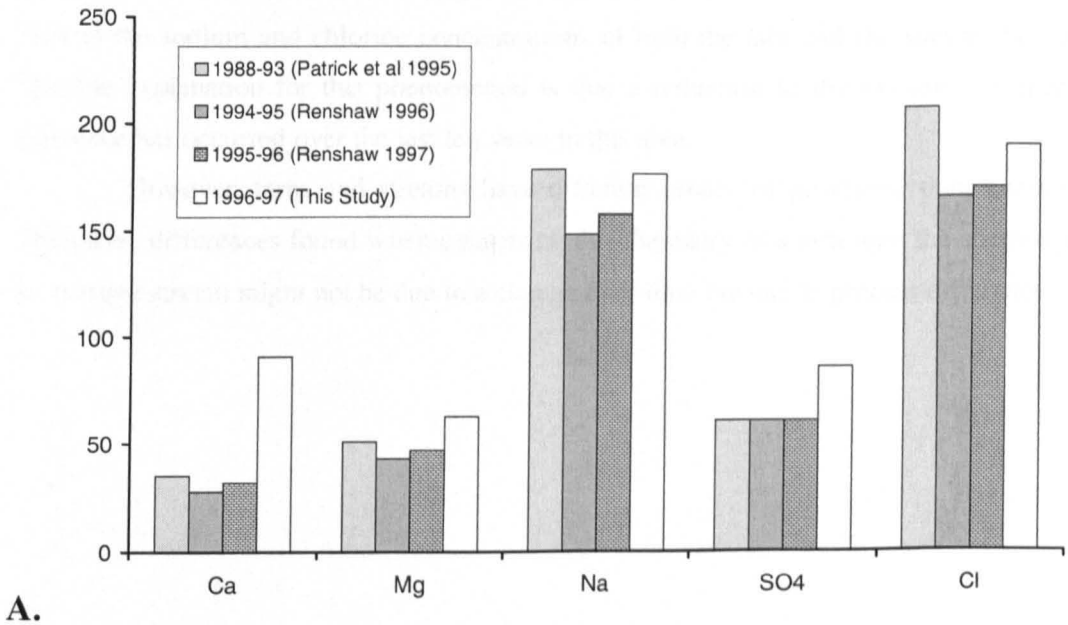
The streams draining the Skiddaw Slate bedrock have very similar base cation, sulphate, nitrate and alkalinity concentrations to the tarns (Figure D15). The highest calcium concentrations are in the streams, whilst the highest magnesium concentrations are in the tarns, although the sum of base cations are similar. This possibly suggests a similar base cation supply from the fairly homogenous bedrock. The tarns have a larger marine influence than the streams indicated by elevated sodium and chloride concentrations.

D.4.3 Comparing tarn and outflow stream chemistry

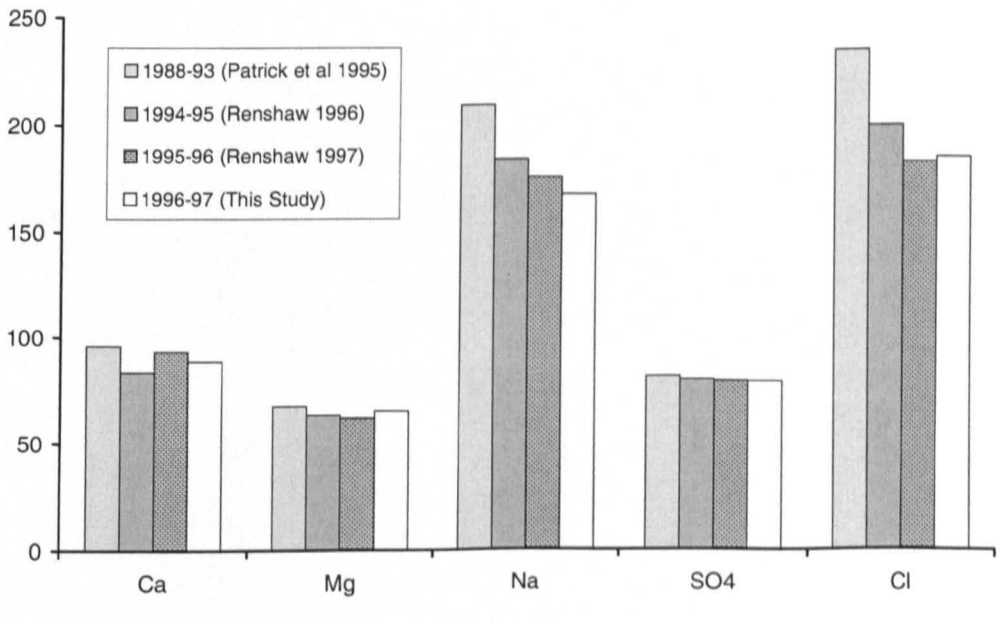
The third 'look and see' exercise compares historical tarn data with the current data from the outflow stream data. The Acid Waters Monitoring Network sampled two tarns on a monthly basis between April 1988 and March 1996. Scoat Tarn is located on Borrowdale Volcanic bedrock, and Burnmoor Tarn is located on Granite bedrock. The survey was initiated to assess the effects of acid deposition across the UK on water bodies receiving different loads of acid rain and with different sensitivities (i.e. ability to buffer acid rain). The published literature covers several time periods, 1988-93 (Patrick *et al.*, 1995), 1994-95 (Renshaw, 1996) and 1995-96 (Renshaw, 1997). The literature provides mean concentrations of pH, calcium, magnesium, potassium, sodium, chloride and sulphate for each site, as well

as data for epilithic diatoms, macrophytes, macroinvertebrates, fish and lake sediments (i.e. palaeoecology). During the course of the current study, the streamwater chemistry of the outflow streams from these tarns was monitored. The data from the AWMN was compared with the data from the current study to ascertain if some historical change in water chemistry had occurred (Figure D16).

Figure D16 - (A) Comparison of AWMN data (1988-96) for Scoat Tarn with current streamwater chemistry for Nether Beck, and (B) Comparison of AWMN data (1988-96) for Burnmoor Tarn with current streamwater chemistry for Whillan Beck. (Units are $\mu eq\ l^{-1}$)



A.



B.

The majority of ion concentrations show little variation between Scoat Tarn and its outflow stream, Nether Beck (Figure D16a). However, the exception is the calcium concentration, which seems to be significantly higher in Nether Beck. The probable explanation for this is that the stream crosses a catchment source of calcium between the tarn and the stream sampling point. This is probably a valid assumption since the stream travels approximately 5 kilometres and has numerous tributaries entering the main channel between the two sampling points.

The majority of ion concentrations are very similar between Burnmoor Tarn and its outflow stream, Whillan Beck (Figure D16b). However, there seems to be a decline over time in the sodium and chloride concentrations of both the tarn and the stream. The most sensible explanation for this phenomenon is that a reduction in the sea-salt (i.e. marine) influence has occurred over the last ten years in this area.

However, tarns and streams have different processes governing their chemistry. Therefore, differences found when comparing the chemistry of a tarn with the chemistry of its outflow stream might not be due to a change over time but due to process differences.

APPENDIX E

Major & Trace Element Data

E.1 XRF Analysis – Major element data

Table E1 – Major element data from the fresh fraction of the rock sample

(Units are wt %)

Sample	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	Total
Rydal Beck	65.83	0.722	15.15	4.50	0.113	1.88	2.71	0.23	4.06	0.222	4.58	100.00
Stock Ghyll	56.89	1.303	17.14	7.91	0.169	2.58	3.83	1.61	2.64	0.276	5.99	100.34
How Beck	56.99	0.921	18.06	8.26	0.142	5.22	0.52	1.50	3.91	0.169	4.19	99.88
Dale Park Beck	58.97	0.900	17.47	7.38	0.075	4.51	0.25	1.60	3.89	0.194	6.05	101.29
Low Cunsey Beck	58.70	0.849	15.40	6.85	0.158	4.06	3.69	1.91	3.14	0.166	4.01	98.93
Belle Grange Beck	67.77	0.706	12.14	4.29	0.063	2.62	2.40	2.76	2.46	0.142	6.39	101.74
Red Dell Beck	62.98	0.606	14.65	3.44	0.174	1.27	5.52	0.22	4.76	0.152	4.66	98.43
Torver Beck	58.71	0.734	14.41	5.81	0.069	3.20	4.72	1.53	3.51	0.148	5.79	98.63
Washfall Beck	64.97	0.855	15.58	6.24	0.124	0.98	0.45	2.71	4.61	0.224	2.02	98.76
Mill Beck 1	61.66	0.870	15.83	6.64	0.058	3.75	0.21	1.70	3.40	0.154	3.95	98.22
Stony Beck	69.64	0.656	14.20	5.18	0.062	1.28	0.41	2.85	2.32	0.154	2.33	99.08
Hagg Gill	70.64	0.456	9.54	4.86	0.254	1.40	3.51	0.07	2.86	0.116	4.97	98.68
Trout Beck	49.77	1.214	14.01	9.38	0.309	3.36	8.40	0.79	1.98	0.306	9.72	99.24
Woundale Beck	52.85	1.397	16.40	8.22	0.235	3.04	5.43	1.29	2.73	0.361	7.25	99.20
Hall Gill	62.60	0.771	16.96	5.16	0.109	1.37	0.55	3.40	3.09	0.200	2.51	96.72
Chapel Beck	61.17	0.893	16.61	7.02	0.073	4.09	0.22	1.53	3.65	0.165	3.92	99.34
Chapel Beck Trib	57.23	0.876	16.97	7.35	0.112	4.41	2.43	1.42	3.92	0.160	5.63	100.51
Grayrigg Hall Beck	0.00	0.030	0.28	1.06	0.178	20.00	29.62	0.08	0.10	0.022	46.76	98.13
St Sundays Beck	69.71	0.651	11.45	4.13	0.068	2.34	2.83	2.48	2.36	0.154	4.05	100.22
Killington Res Trib	70.22	0.732	10.01	3.61	0.065	1.92	4.19	2.29	2.13	0.154	4.76	100.08
River Mint Trib	69.14	0.735	12.52	4.80	0.053	2.86	1.25	2.20	2.64	0.150	3.27	99.62
Borrow Beck	61.18	0.844	15.63	6.65	0.091	4.09	2.01	1.85	3.35	0.168	4.66	100.52
Bannisdale Beck	65.86	0.607	11.27	4.47	0.099	2.52	4.64	2.20	2.28	0.114	5.69	99.75
River Sprint	52.19	1.231	16.96	7.86	0.163	4.24	5.51	3.43	2.16	0.307	6.72	100.77
Moasdale Beck	62.69	0.878	18.01	6.35	0.177	2.36	1.15	3.33	3.14	0.230	2.24	100.56
Castle How Beck	60.66	0.913	17.38	6.38	0.161	1.59	4.20	2.97	4.23	0.232	1.91	100.63
Tarn Beck	67.24	0.814	14.21	7.63	0.189	2.76	0.75	2.31	1.82	0.211	2.88	100.81
Sling Beck	59.73	0.871	18.66	5.79	0.153	2.86	1.91	4.73	3.57	0.273	2.19	100.74
Holehouse Gill	55.48	0.968	16.28	7.85	0.190	4.85	3.73	1.69	2.71	0.240	6.41	100.40
Greendale Gill	61.65	0.825	17.36	5.51	0.072	1.95	3.91	3.48	3.35	0.300	1.86	100.27
Nether Beck	61.87	0.820	18.85	4.50	0.044	1.65	3.09	7.53	0.45	0.300	1.49	100.59
Whillan Beck	78.61	0.107	13.08	0.60	0.018	0.16	0.38	3.77	2.40	0.208	1.16	100.49
Hardknott Gill	63.22	0.837	17.87	5.72	0.095	2.94	1.62	1.25	3.74	0.277	3.13	100.70
Whelpside Ghyll	69.43	0.315	15.18	2.65	0.051	0.35	0.44	2.76	5.06	0.309	1.41	97.96
Wyth Burn	58.16	0.763	15.88	5.98	0.172	2.14	4.89	0.83	4.03	0.230	6.60	99.68
Launchy Ghyll	54.21	0.837	19.23	6.69	0.189	2.63	3.50	2.95	3.26	0.251	5.74	99.49
Shoulthwaite Gill	51.63	1.194	17.91	10.99	0.280	4.72	2.93	2.94	2.26	0.185	4.20	99.24
Coledale Beck	52.92	1.081	23.92	9.89	0.477	1.78	0.27	0.79	3.00	0.217	5.16	99.51
Liza Beck	57.32	1.156	22.04	7.86	0.071	1.73	0.62	1.00	3.17	0.371	3.99	99.33
Mill Beck 2	51.57	1.192	24.23	11.17	0.541	1.92	0.22	1.23	2.96	0.191	5.16	100.38
Sour Milk Gill	57.27	0.787	16.26	5.11	0.148	1.30	5.41	2.82	2.85	0.271	6.22	98.45
Styhead Gill	54.64	0.837	17.74	5.71	0.164	1.72	5.34	2.44	3.41	0.304	5.92	98.23
Glenridding Beck	57.06	0.869	17.35	6.29	0.186	2.25	3.40	1.36	3.41	0.185	5.86	98.22
Glencoyne Beck	67.54	0.430	16.97	3.79	0.092	0.94	0.93	1.57	3.16	0.270	3.22	98.91
Aira Beck	58.00	0.856	18.06	8.89	0.285	1.20	4.46	2.38	3.15	0.179	2.97	100.43
Fusedale Beck	69.05	0.329	16.14	4.12	0.019	0.87	0.44	0.78	5.28	0.361	2.72	100.11
Heltondale Beck	60.41	0.936	17.46	6.22	0.195	3.22	1.77	2.78	2.44	0.203	4.45	100.08
Cawdale Beck	54.55	1.240	15.97	9.69	0.191	2.29	5.13	3.04	1.69	0.208	6.48	100.48
Gatescarth Beck	59.97	0.952	15.67	6.67	0.187	2.83	3.61	1.50	2.82	0.190	5.65	100.05
Naddle Beck	63.13	0.926	15.07	5.35	0.206	3.30	1.95	0.08	3.72	0.167	5.55	99.45
Mosedale Beck	62.02	0.948	16.19	6.20	0.181	2.27	2.37	3.47	1.53	0.167	4.16	99.51
Tailbert Gill	59.18	0.763	15.31	6.21	0.186	3.82	4.72	3.68	1.52	0.135	4.59	100.11

Table E2 – Major element data from the weathered fraction of the rock sample

(Units are wt %)

Sample	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	Total
Rydal Beck	69.11	0.741	15.60	4.18	0.100	1.73	0.52	0.17	4.30	0.222	3.28	99.95
Stock Ghyll	58.63	1.375	18.12	8.05	0.144	2.51	1.83	1.60	2.86	0.298	5.04	100.46
How Beck	56.32	0.922	18.23	8.35	0.100	5.18	0.27	1.42	3.97	0.168	4.71	99.64
Dale Park Beck	59.30	0.974	18.01	7.48	0.079	4.31	0.22	1.43	4.30	0.187	4.56	100.85
Low Cunsey Beck	58.94	0.877	16.27	7.22	0.118	4.24	1.19	1.82	3.41	0.159	4.89	99.13
Belle Grange Beck	71.93	0.773	12.28	3.88	0.063	2.10	0.74	2.70	2.69	0.157	3.00	100.31
Red Dell Beck	62.50	0.616	14.87	3.61	0.174	1.33	4.79	0.07	4.67	0.147	6.31	99.09
Torver Beck	59.23	0.763	14.72	5.92	0.068	3.20	3.72	1.76	3.54	0.138	5.70	98.76
Washfall Beck	65.01	0.861	15.87	7.14	0.131	1.06	0.45	2.52	4.78	0.221	2.22	100.26
Mill Beck 1	60.91	0.873	16.22	6.90	0.073	3.90	0.17	1.62	3.49	0.146	4.28	98.58
Stony Beck	67.36	0.660	15.32	5.21	0.064	1.27	0.46	3.14	2.34	0.161	2.34	98.33
Hagg Gill	74.74	0.471	10.43	5.85	0.168	1.53	0.14	0.05	2.99	0.135	3.16	99.66
Trout Beck	52.38	1.291	15.07	10.58	0.327	3.79	5.34	0.76	1.98	0.327	7.85	99.70
Woundale Beck	53.30	1.413	16.39	8.26	0.248	2.85	2.34	1.13	2.78	0.346	5.59	94.65
Hall Gill	64.14	0.809	16.90	4.83	0.086	1.27	0.47	3.53	3.14	0.202	2.80	98.18
Chapel Beck	61.05	0.881	16.74	7.19	0.082	4.23	0.18	1.42	3.72	0.151	4.29	99.93
Chapel Beck Trib	58.47	0.847	16.22	6.98	0.165	3.95	1.93	1.56	3.66	0.158	5.52	99.46
Grayrigg Hall Beck	0.19	0.030	0.36	1.20	0.194	20.64	30.52	0.06	0.12	0.022	46.70	100.04
St Sundays Beck	70.21	0.666	11.85	4.33	0.066	2.37	1.51	2.41	2.48	0.160	3.23	99.28
Killington Res Trib	73.79	0.750	10.41	4.12	0.054	1.90	1.54	2.36	2.26	0.162	3.13	100.48
River Mint Trib	70.52	0.750	12.35	4.62	0.048	2.74	0.79	2.14	2.66	0.152	3.09	99.86
Borrow Beck	60.95	0.846	15.31	6.58	0.085	3.97	1.28	1.85	3.30	0.166	5.67	100.01
Bannisdale Beck	68.37	0.624	11.34	4.41	0.099	2.44	2.55	2.25	2.36	0.125	4.53	99.10
River Sprint	52.33	1.385	18.72	8.91	0.169	4.70	1.73	3.36	2.50	0.350	4.71	98.86
Moasdale Beck	62.43	0.911	17.72	6.15	0.159	2.14	1.06	2.88	3.42	0.204	2.80	99.87
Castle How Beck	59.13	0.957	17.48	6.55	0.166	1.53	5.09	2.40	4.15	0.227	2.14	99.82
Tarn Beck	61.21	0.863	16.33	9.18	0.235	3.30	0.78	2.05	2.27	0.212	3.48	99.91
Sling Beck	59.44	0.911	18.62	5.38	0.150	2.50	1.95	4.99	3.60	0.258	2.31	100.11
Holehouse Gill	55.91	1.008	16.87	8.24	0.190	5.01	2.40	1.80	2.83	0.244	5.77	100.27
Greendale Gill	61.40	0.821	17.16	5.28	0.068	1.86	4.15	3.22	3.38	0.289	2.14	99.77
Nether Beck	62.16	0.845	18.71	4.29	0.041	1.59	2.90	7.43	0.48	0.265	1.74	100.45
Whillan Beck	80.14	0.097	11.80	0.59	0.014	0.15	0.33	2.54	3.22	0.202	1.02	100.10
Hardknott Gill	62.48	0.832	17.64	5.86	0.101	3.02	0.95	1.09	4.29	0.238	3.38	99.88
Whelpside Ghyll	71.48	0.327	15.17	2.29	0.045	0.38	0.42	2.81	5.32	0.315	1.39	99.95
Wyth Burn	59.51	0.872	16.47	6.79	0.167	2.45	2.47	1.06	3.93	0.226	5.22	99.17
Launchy Ghyll	55.72	0.778	18.60	7.01	0.201	2.73	3.13	2.91	3.15	0.260	5.57	100.06
Shoulthwaite Gill	53.49	1.264	17.67	10.42	0.293	4.54	2.88	3.12	2.33	0.198	4.18	100.39
Coledale Beck	56.29	0.932	21.08	10.41	0.484	1.71	0.25	0.73	2.55	0.218	4.99	99.64
Liza Beck	59.30	1.201	21.88	6.58	0.056	1.44	0.52	1.06	3.35	0.301	4.27	99.96
Mill Beck 2	52.64	1.201	23.00	10.51	0.503	1.78	0.21	1.17	2.98	0.182	5.47	99.65
Sour Milk Gill	62.43	0.866	17.37	5.44	0.127	1.39	1.86	2.95	3.12	0.270	4.24	100.06
Styhead Gill	58.32	0.889	18.35	5.94	0.131	1.77	3.10	2.43	3.63	0.307	5.03	99.90
Glenridding Beck	60.80	0.966	18.44	6.92	0.233	2.34	0.79	1.46	3.67	0.198	4.15	99.97
Glencoyne Beck	68.00	0.450	17.69	3.77	0.087	0.95	0.40	1.48	3.42	0.268	3.17	99.69
Aira Beck	61.04	0.846	17.85	7.14	0.191	0.85	3.82	2.28	3.47	0.180	1.99	99.66
Fusedale Beck	68.20	0.336	16.16	4.15	0.021	0.86	0.39	0.48	5.52	0.348	3.44	99.91
Heltondale Beck	60.59	0.974	17.75	6.55	0.213	3.29	1.14	3.08	2.31	0.202	4.12	100.22
Cawdale Beck	56.46	1.289	16.24	11.25	0.194	2.17	2.08	2.94	1.78	0.211	5.54	100.15
Gatescarth Beck	63.46	0.990	15.83	6.35	0.138	2.64	1.21	1.47	3.02	0.178	4.49	99.78
Naddle Beck	68.55	0.896	13.90	5.14	0.187	2.39	0.80	0.10	3.49	0.162	3.92	99.54
Mosedale Beck	65.55	1.032	15.79	5.40	0.150	1.86	1.07	3.60	1.66	0.160	3.54	99.81
Tailbert Gill	63.35	0.902	14.65	6.10	0.169	3.19	2.23	3.55	1.77	0.167	3.76	99.84

E.2 XRF Analysis – Trace element data

Table E3 – Trace element data from the fresh fraction of the rock sample

(Units are ppm)

Sample	Rb	Sr	Y	Zr	Ba	Pb	Sc	V	Cr	Co	Ni	Cu	Zn
Rydal Beck	163	52.3	38.4	250	612	24	13	60	11	6	6	8	66
Stock Ghyll	99.5	133	33.8	157	462	8	26	243	29	17	10	21	84
How Beck	160	53.5	31.3	161	567	13	20	156	164	28	110	36	138
Dale Park Beck	164	48.3	22.9	182	728	11	18	153	168	24	108	26	104
Low Cunsey Beck	119	118	29.2	196	454	16	18	123	218	23	87	30	96
Belle Grange Beck	84	164	26.8	229	524	13	12	85	109	13	53	18	68
Red Dell Beck	225	63.7	41.0	183	671	19	19	73	98	12	13	10	71
Torver Beck	138	147	29.4	197	538	37	14	104	106	19	67	26	137
Washfall Beck	162	215	33.0	250	827	9	20	66	21	9	9	8	66
Mill Beck 1	135	48	31.5	241	520	28	16	124	160	23	89	26	97
Stony Beck	94	142	42.4	234	586	11	18	40	11	5	2	4	105
Hagg Gill	97.2	89.9	32.3	162	391	9	11	48	31	8	19	10	54
Trout Beck	79	173	30.7	151	377	7	33	224	45	19	6	5	105
Woundale Beck	110	132	33.4	174	541	9	35	256	55	17	8	4	87
Hall Gill	142	148	47.7	324	931	11	23	40	7	6	3	5	73
Chapel Beck	144	42.9	35.9	233	529	17	18	129	165	26	100	33	98
Chapel Beck Trib	163	88.1	28.0	184	527	17	22	147	168	25	101	37	113
Grayrigg Hall Beck	3.7	56.3	2.4	8	5	3	11	8	5	3	4	1	4
St Sundays Beck	81.2	150	26.3	199	440	31	10	73	94	15	54	10	61
Killington Res Trib	69.1	160	33.1	382	367	7	9	65	124	13	42	8	47
River Mint Trib	96.6	104	28.8	249	480	15	9	84	127	15	61	16	68
Borrow Beck	136	95.1	35.0	223	515	19	16	122	160	23	88	30	95
Bannisdale Beck	78	174	28.3	175	434	10	10	69	89	15	56	18	62
River Sprint	54.5	197	26.1	148	450	4	24	225	88	21	36	14	81
Moasdale Beck	139	196.7	38.2	247	956	2	12	77	45	17	21	18	34
Castle How Beck	107	187.4	40.1	275	613	4	17	103	30	10	10	5	24
Tarn Beck	95	50.9	24.8	210	222	2	13	103	40	14	14	3	59
Sling Beck	102	236.7	33.2	221	1514	0	12	89	49	14	18	2	38
Holehouse Gill	117	106.6	30.9	180	685	9	27	172	282	29	76	58	100
Greendale Gill	118	253.7	48.9	252	952	3	15	75	30	15	10	2	22
Nether Beck	15.1	321.8	39.0	236	88	2	14	53	21	13	5	2	9
Whillan Beck	150	29.4	11.2	68	101	4	0	2	9	2	2	2	8
Hardknott Gill	156	132.6	32.9	238	373	3	11	74	37	14	17	29	32
Whelpside Ghyll	201	82.4	62.4	342	911	6	16	5	6	3	3	12	19
Wyth Burn	202	61.3	44.6	186	694	15	26	109	60	15	15	31	74
Launchy Ghyll	152	102	46.5	221	1214	7	19	90	145	16	20	7	73
Shoulthwaite Gill	79.7	208	30.0	160	511	7	29	203	134	29	30	21	128
Coledale Beck	156	107	31.4	152	599	9	21	143	170	9	54	16	110
Liza Beck	152	133	46.2	209	641	395	22	158	125	10	26	29	400
Mill Beck 2	147	154	30.2	170	661	15	27	162	150	32	60	29	98
Sour Milk Gill	120	162	46.1	245	645	7	19	72	18	10	9	57	62
Styhead Gill	136	199	32.3	202	677	4	19	92	27	13	12	7	69
Glenridding Beck	145	72.6	36.9	156	867	13	18	126	135	19	18	22	78
Glencoyne Beck	159	80.1	67.6	249	470	28	11	24	43	5	7	11	70
Aira Beck	117	216.9	47.8	164	1122	18	26	81	22	17	8	18	105
Fusedale Beck	203	36.4	63.2	315	705	2	18	18	16	2	4	4	55
Heltondale Beck	102	77.5	35.0	191	500	7	20	149	113	23	33	33	73
Cawdale Beck	58.4	93.2	28.1	146	359	2	30	258	175	26	13	30	88
Gatescarth Beck	113	76.4	29.0	162	415	15	21	112	80	17	56	27	84
Naddle Beck	171	12.7	32.4	197	609	5	17	116	58	16	19	42	61
Mosedale Beck	68	202	32.5	207	431	18	18	104	45	14	18	23	77
Tailbert Gill	32.3	232	23.7	151	510	11	17	148	136	19	36	32	66

Table E4 – Trace element data from the weathered fraction of the rock sample

(Units are ppm)

Sample	Rb	Sr	Y	Zr	Ba	Pb	Sc	V	Cr	Co	Ni	Cu	Zn
Rydal Beck	171	28.6	36.4	259	677	31	13	53	11	8	7	8	66
Stock Ghyll	108.2	115	32.7	170	522	20	30	261	28	24	9	19	91
How Beck	165	46.2	29.9	159	581	19	19	160	163	27	113	32	153
Dale Park Beck	189	43.4	21.0	191	605	22	19	161	173	24	96	18	89
Low Cunsey Beck	138.5	73.2	29.3	204	514	21	16	137	168	23	97	32	107
Belle Grange Beck	98.9	132	19.9	248	559	30	11	83	101	10	43	11	45
Red Dell Beck	227	59	43.2	189	693	25	18	76	118	8	12	12	82
Torver Beck	140	130	31.3	217	631	44	15	105	110	18	67	29	182
Washfall Beck	169	218	31.5	256	844	11	23	70	28	8	9	8	72
Mill Beck 1	142	45	27.5	232	530	29	16	127	154	23	91	26	95
Stony Beck	96.3	171	38.0	248	577	11	17	41	8	4	4	3	101
Hagg Gill	108	12	27.3	162	414	10	11	52	24	7	20	10	73
Trout Beck	78.5	124	33.7	161	424	9	33	229	49	22	9	6	147
Woundale Beck	116	99	33.1	182	667	12	34	264	57	17	7	6	102
Hall Gill	144	148	34.6	342	911	20	18	34	5	6	3	4	62
Chapel Beck	149	39.1	24.2	216	531	15	18	131	163	23	100	30	93
Chapel Beck Trib	154	82.9	29.0	187	548	22	17	138	159	23	96	29	129
Grayrigg Hall Beck	4.1	61.9	1.8	8	13	3	13	7	4	3	5	4	5
St Sundays Beck	87.8	121	24.8	197	459	29	12	71	97	15	55	11	66
Killington Res Trib	73	112	27.5	356	404	10	9	64	117	13	45	9	51
River Mint Trib	97.4	92	25.6	259	473	17	11	83	120	12	59	15	64
Borrow Beck	138	88.1	37.2	234	638	17	17	124	154	20	92	31	118
Bannisdale Beck	82.8	130	25.8	164	469	22	9	66	89	14	53	16	77
River Sprint	66.1	158	25.2	171	549	15	25	264	109	27	40	9	100
Moasdale Beck	155	175.7	31.4	255	1054	15	13	76	47	14	20	15	32
Castle How Beck	111	188.9	41.8	291	570	11	18	109	25	9	9	5	26
Tarn Beck	120	52.5	27.3	222	302	3	20	132	58	16	14	5	79
Sling Beck	101	247	32.7	235	1593	9	14	93	46	13	17	3	34
Holehouse Gill	122	89.1	31.2	188	716	17	27	180	288	27	84	49	113
Greendale Gill	118	269.3	44.9	251	984	2	16	71	24	12	11	4	21
Nether Beck	17.4	315.9	35.8	242	88	12	15	54	13	11	5	2	7
Whillan Beck	183	26.4	12.1	66	148	4	1	2	5	1	3	2	9
Hardknott Gill	184	115.8	28.9	238	461	1	10	68	37	17	19	48	36
Whelpside Ghyll	209	81.1	65.7	340	932	10	16	7	7	4	3	9	17
Wyth Burn	200	45.5	35.2	185	718	34	25	141	36	16	15	23	105
Launchy Ghyll	144	96.2	45.1	208	845	9	18	88	21	16	18	7	78
Shoulthwaite Gill	82.1	213	30.6	155	563	11	30	208	261	32	27	20	137
Coledale Beck	131	95.2	29.1	123	494	43	16	124	110	25	53	37	118
Liza Beck	167	140	47.2	216	689	541	19	155	116	6	17	8	86
Mill Beck 2	151	146	31.3	173	666	20	25	161	153	35	55	27	91
Sour Milk Gill	132	121	43.7	263	769	9	18	77	20	8	11	52	71
Styhead Gill	145	171	32.2	214	741	7	19	99	32	14	14	11	78
Glenridding Beck	155	53.7	34.5	168	912	56	21	130	57	22	19	20	83
Glencoyne Beck	170	75	56.4	255	529	27	13	27	35	6	6	10	65
Aira Beck	131	215.9	43.5	165	1250	20	22	77	15	12	4	17	78
Fusedale Beck	215	28.7	63.0	334	735	12	17	20	39	3	5	5	52
Heltondale Beck	94.3	83.5	35.6	197	490	7	21	161	116	21	31	32	80
Cawdale Beck	62.3	72.8	30.0	160	386	17	35	269	37	30	12	30	94
Gatescarth Beck	121	49.4	26.6	170	464	23	18	112	75	15	48	20	78
Naddle Beck	159	10.8	28.8	190	619	6	16	105	52	17	19	57	84
Mosedale Beck	76.5	191	31.1	222	473	28	18	106	44	11	15	17	61
Tailbert Gill	45.5	231	23.4	175	649	23	19	159	113	19	33	28	59

APPENDIX F

Catchment Characteristics Data

F.1 ARC/Info and Catchment digitisation – Full details

Catchment characteristics are used in Chapter 4 and 5 as part of the data analyses. Here a more detailed discussion takes place of the method behind obtaining the catchment characteristics as proportions per catchment.

F.1.1 Identifying the experimental catchments

Initially a plot of the rivers falling within the designated area of the Lake District (SW corner 315490, NE corner 360525) was created using the *Institute of Hydrology Digital Terrane Model (IHDTM).* A mapping package called *Degener8* was used to create a hard copy of the chosen area's rivers and contour lines. The hard copy was overlaid manually over a 1:50,000 geology map held in the library at BGS Keyworth. Approximately 100 streams were then chosen on the basis of the geological range deemed to fall within the rivers catchment area. The role of geology is considered important in the stream's water chemistry so catchments with single geological units as well as those with several geological units were selected. Subsequently, these 100 streams were located on 1:25,000 Gridranger Ordinance Survey maps.

For the purpose of this study, the original 100 sites were reduced to 55 due to time and resource constraints, and not unimportantly upon the accessibility of the sites by car. This reduction of sites was necessary and hopefully has not caused an adverse bearing on the results of the study. The grid references of the sites was finalised after a field reconnaissance exercise was carried out in March 1996.

F.1.2 Generating catchment boundaries

The grid references from the 1:25,000 O/S maps were entered into a program called *Gridlook* - which allows you to view many kinds of gridded data in a number of different text formats. For the purpose of this study the program was used for locating *IHDTM* grid references, which are required to a resolution of 50 metres. Once the grid references had been derived they were entered into *Tstcd* - a program for generating a catchment boundary

and estimating catchment runoff. Once all 55 catchments had been generated in *Tstcd* they were saved in Arc/Info ungenerated format for use later.

F.1.3 Catchment Characteristic data

a. Geology data

The original basis of the catchment selection was the geology derived from 1:50,000 geology maps. However, since the maps are held under licence by BGS direct copying and subsequent digitisation of the maps is prohibited. However, BGS agreed to supply a copy of the 1:250,000 scale solid geological data of the area in digital format. This digital data used the BGS 1:250k published solid geology maps as the source digitising document. The maps display an inconsistency in the geological classifications of strata. The very nature of geological mapping means that the information presented is an interpretation of the facts and observations carried out in the compilation of the particular map. However, the dataset should be adequate for the purposes of this thesis and the subsequent XRF analysis provides a more in depth geological basis for the model.

b. Land Cover data

The Land Cover Map of Great Britain was produced using supervised maximum likelihood classifications of Landsat Thematic Mapper data. The map is based on a 25m grid and records 25 cover types. (Fuller *et al*, 1984). The combination of summer and winter data substantially improved the classification's accuracy (Fuller *et al*, 1994).

The Environmental Information Centre at the Institute of Terrestrial Ecology (Monks Wood) provided a map in Arc/Info format showing the dominant land cover class for each 1km square of the chosen area. The land cover classes are:

1 = sea / estuary
2 = inland water
3 = coastal bare ground
4 = saltmarsh
5 = lowland grass heath
6 = pasture / amenity turf
7 = meadows
8 = marsh / rough grassland
9 = montane / hill grass
10 = dwarf shrub / grass moorland
11 = upland dwarf shrub moorland
12 = bracken
13 = lowland heath
14 = scrub / orchard
15 = deciduous wood
16 = coniferous wood
17 = upland bogs
18 = arable / tilled land
19 = ruderal weeds
20 = suburban
21 = urban
22 = bare ground
23 = felled forest
24 = lowland bogs
25 = dwarf shrub / grass heath

c. Deposition data

The Environmental Information Centre at the Institute of Terrestrial Ecology (Monks Wood) provided a map in Arc/Info format showing the mean deposition data for 1989-92 for the chosen area. Stations set up by Warren Springs Laboratory measure the amount of wet and dry and cloud deposition. The ITE map covers deposition at a resolution of 20km based on the findings of the Warren Springs stations. The attributes measured in keq/ha/year are:

nms = non-marine sulphur
tots = non-marine plus marine sulphur
nox = oxidised nitrogen
nhx = reduced nitrogen
nmbc = non-marine base cations (Ca+Mg)
totbc = non-marine plus marine base cations (Ca+Mg)

d. Hydrology of Soil Types (HOST) data

The *HOST* classification is ideal for the estimation of hydrological parameters within catchments. The *HOST* data set is obtained by applying the classification to the soils of the national maps as represented on a 1km grid. Firstly, soil units in each 1km from Soil Survey's 1:250,000 soil maps were identified, then the classification was applied as the sum of the percentages across all map units (Boorman *et al*, 1995). By far the most accurate utilisation of the system is using a manual overlay procedure, but this is also the most tiresome.

Digital versions of the classification hand the task to a computer. However, when a catchment boundary cuts through a square the proportion of the square is found, and the all classes are calculated based on the assumption that distribution in this portion is the same as the whole square. For this reason some care may need to be taken with small catchments.

The *HOST* classification for the chosen area was generated as a grid in Arc/Info and provided by the Institute of Hydrology at the 1km scale. Within each 1km grid square the percentage of each *HOST* soil type is listed.

F.1.4 Using the Arc/Info program

Arc/Info is a geographic information system with tools for automation, analysis and management of geographic information and was developed by Environmental Systems Research Institute Inc. (ESRI).

The easiest way to use Arc/Info is to use the Arc Macro Language (AML). This powerful tool allows you to build macros to automate frequently performed command sequences which saves retyping each time a command needs to be executed.

The catchment boundaries created by *Tstcd* were entered into Arc/Info by generating a new cover (using the command **generate**). However, since the boundaries were created separately some display the same watersheds so Arc/Info thought that the data points were erroneous. To rectify this the **build** command was used to remove the overlapping lines.

The new coverage contained all 55 catchments. To calculate the proportion of each attribute each catchment needed to be treated as a separate polygon. The catchments were labelled by grid reference. They were turned into individual polygons for Arc/Info using the **reselect** and **writeselect** commands. Each catchment was called Catch and then the catchment number (i.e. catch54).

Land Cover and Deposition

Using the command **latticeclip** the catchments were overlaid on the deposition and the land cover data. This formed distinct polygons containing the deposition and land cover data for each discrete catchment (i.e. dep54 and land54 respectively). In order to ascertain the percentages within each catchment it was necessary to carry out statistics on each catchment (using the **sum** command). For ease, each class of land cover and deposition type was put into an AML macro. The catchment then had to be brought up individually and the AML executed for each catchment. This gave the percentage of each land class and deposition in each individual catchment. Once this procedure had been carried out on the 55 catchments, deposition and land cover proportions were known for each individual catchment (Full details in Appendix F.2).

Geology and HOST

The method used for the geology and the *HOST* data was slightly different. By using the **identity** command the geometric intersection of two coverage's can be computed. All features of the input coverage (i.e. the catchment) as well as those of the identity coverage (i.e. the geology or soil) are preserved in the output coverage. All 55 catchments were

overlaid on the geology data and then the *HOST* data as a single coverage. Individual catchments were then "lifted" from the coverage by using **reselect** and the catchment label. In order to find the percentages in each catchment the **list** command was used for each successive polygon. Once all 55 polygons had been through the procedure of "lifting" and having their contents listed, the proportions of the geology and *HOST* classification soil types were known for each individual catchment (Full details in Appendix F.2).

F.2 Catchment characteristics – Full details

Table F1 – Percentage areal coverage of the rock types in the study catchments

Sample	Andesite	Tuff	Rhyolite	Skiddaw	Granite	Silurian Siltstone	Silurian Greywacke	Silurian Mudstone	Coniston Limest	Basalt	Carbonif Limest
Rydal Beck	5	94	1	0	0	0	0	0	0	0	0
Stock Ghyll	10	90	0	0	0	0	0	0	0	0	0
How Beck	0	0	0	0	0	0	100	0	0	0	0
Dale Park Beck	0	0	0	0	0	0	0	100	0	0	0
Low Cunsey Beck	0	0	0	0	0	0	0	100	0	0	0
Belle Grange Beck	0	0	0	0	0	0	85	15	0	0	0
Red Dell Beck	5	33	62	0	0	0	0	0	0	0	0
Torver Beck	8	48	3	0	0	41	0	0	0	0	0
Washfall Beck	8	92	0	0	0	0	0	0	0	0	0
Mill Beck 1	0	0	0	0	0	0	9	91	0	0	0
Stony Beck	0	74	26	0	0	0	0	0	0	0	0
Hagg Gill	41	59	0	0	0	0	0	0	0	0	0
Trout Beck	18	82	0	0	0	0	0	0	0	0	0
Woundale Beck	20	80	0	0	0	0	0	0	0	0	0
Hall Gill	59	0	0	0	0	0	0	0	41	0	0
Chapel Beck	0	0	0	0	0	0	0	100	0	0	0
Chapel Beck Trib	0	0	0	0	0	0	0	100	0	0	0
Grayrigg Hall Beck	0	0	0	0	0	0	75	13	0	0	12
Flodder Beck	0	0	0	0	0	0	38	62	0	0	0
St Sundays Beck	0	0	0	0	0	0	100	0	0	0	0
Killington Res Trib	0	0	0	0	0	10	90	0	0	0	0
River Mint Trib	0	0	0	0	0	0	100	0	0	0	0
Borrow Beck	0	0	2	0	0	0	27	47	24	0	0
Bannisdale Beck	0	0	0	0	0	0	60	0	40	0	0
River Sprint	85	15	0	0	0	0	0	0	0	0	0
Moasdale Beck	28	72	0	0	0	0	0	0	0	0	0
Castle How Beck	68	32	0	0	0	0	0	0	0	0	0
Tarn Beck	27	73	0	0	0	0	0	0	0	0	0
Sling Beck	0	100	0	0	0	0	0	0	0	0	0
Holehouse Gill	9	87	4	0	0	0	0	0	0	0	0
Crosby Gill	25	72	3	0	0	0	0	0	0	0	0
Greendale Gill	46	0	0	0	55	0	0	0	0	0	0
Nether Beck	39	34	0	0	28	0	0	0	0	0	0
Whillan Beck	43	19	1	0	38	0	0	0	0	0	0
Hardknott Gill	97	3	0	0	0	0	0	0	0	0	0
Whelpside Ghyll	17	82	1	0	0	0	0	0	0	0	0
Wyth Burn	0	95	5	0	0	0	0	0	0	0	0
Launchy Ghyll	41	53	6	0	0	0	0	0	0	0	0
Shoulthwaite Gill	42	58	0	0	0	0	0	0	0	0	0
Coledale Beck	0	0	0	100	0	0	0	0	0	0	0
Liza Beck	0	0	0	100	0	0	0	0	0	0	0
Mill Beck 2	0	0	0	100	0	0	0	0	0	0	0
Sour Milk Gill	0	91	0	0	10	0	0	0	0	0	0
Styhead Gill	0	96	3	0	1	0	0	0	0	0	0
Glenridding Beck	35	58	7	0	0	0	0	0	0	0	0
Glencoyne Beck	16	59	24	1	0	0	0	0	0	0	0
Aira Beck	2	30	68	0	0	0	0	0	0	0	0
Parkhouse Gill	0	29	21	50	0	0	0	0	0	0	0
Fusedale Beck	0	100	0	0	0	0	0	0	0	0	0
Heltondale Beck	0	94	0	0	0	0	0	0	0	6	0
Cawdale Beck	0	100	0	0	0	0	0	0	0	0	0
Gatescarth Beck	58	42	0	0	0	0	0	0	0	0	0
Naddle Beck	22	52	0	0	26	0	0	0	0	0	0
Mosedale Beck	75	25	0	0	0	0	0	0	0	0	0
Tailbert Gill	100	0	0	0	0	0	0	0	0	0	0

Table F2 – Percentage areal coverage of the Land Cover types in the study catchments

Sample	Hill Grass	Bracken	Moor	Meadow	C.Wood	D.Wood
Rydal Beck	99	0	0	0	0	1
Stock Ghyll	85	12	0	3	0	0
How Beck	0	0	0	77	24	0
Dale Park Beck	0	0	0	0	57	45
Low Cunsey Beck	0	0	0	6	53	43
Belle Grange Beck	0	0	0	14	67	18
Red Dell Beck	99	1	0	0	0	0
Torver Beck	88	3	0	9	0	0
Washfall Beck	100	0	0	0	0	0
Mill Beck 1	0	0	0	100	0	0
Stony Beck	81	0	0	19	0	0
Hagg Gill	59	41	0	0	0	0
Trout Beck	100	0	0	0	0	0
Woundale Beck	92	8	0	0	0	0
Hall Gill	100	0	0	0	0	0
Chapel Beck	0	0	0	100	0	0
Chapel Beck Trib	0	0	0	100	0	0
Grayrigg Hall Beck	15	0	0	85	0	0
Flodder Beck	37	0	0	63	0	0
St Sundays Beck	35	0	0	65	0	0
Killington Res Trib	40	0	0	60	0	0
River Mint Trib	82	0	0	18	0	0
Borrow Beck	100	0	0	0	0	0
Bannisdale Beck	100	0	0	0	0	0
River Sprint	90	10	0	0	0	0
Moasdale Beck	100	0	0	0	0	0
Castle How Beck	78	0	0	0	23	0
Tarn Beck	83	17	0	0	0	0
Sling Beck	97	0	0	3	0	0
Holehouse Gill	100	0	0	0	0	0
Crosby Gill	100	0	0	0	0	0
Greendale Gill	99	1	0	0	0	0
Nether Beck	90	9	0	0	0	0
Whillan Beck	99	1	0	0	0	0
Hardknott Gill	69	31	0	0	0	0
Whelpside Ghyll	92	3	0	0	0	0
Wyth Burn	77	23	0	0	0	0
Launchy Ghyll	45	0	55	0	0	0
Shoulthwaite Gill	70	8	15	0	0	9
Coledale Beck	1	98	0	0	1	0
Liza Beck	19	81	0	0	0	0
Mill Beck 2	32	68	0	0	0	0
Sour Milk Gill	99	1	0	0	0	0
Styhead Gill	43	57	0	0	0	0
Glenridding Beck	57	43	0	0	0	0
Glencoyne Beck	68	32	0	0	0	0
Aira Beck	100	0	0	0	0	0
Parkhouse Gill	62	0	0	35	0	4
Fusedale Beck	55	0	0	45	0	0
Heltondale Beck	79	21	0	0	0	0
Cawdale Beck	58	18	0	24	0	0
Gatescarth Beck	48	52	0	0	0	0
Naddle Beck	99	0	0	1	0	0
Mosedale Beck	100	0	0	0	0	0
Tailbert Gill	88	0	0	12	0	0

Table F3 – Percentage areal coverage of the HOST soil types in the study catchments

Sample	HC4	HC5	HC8	HC9	HC10	HC15	HC17	HC18	HC19	HC21	HC22	HC24	HC26	HC27	HC29	HC98
Rydal Beck	10	0	0	0	0	0	0	0	26	0	0	0	0	36	28	0
Stock Ghyll	4	0	0	0	0	4	0	0	10	0	0	0	19	29	34	0
How Beck	4	0	0	0	0	8	20	4	0	0	4	0	37	0	22	0
Dale Park Beck	2	0	0	0	0	7	26	2	0	0	4	0	36	0	22	1
Low Cunsey Beck	4	0	0	0	0	7	18	4	0	0	4	0	37	0	22	4
Belle Grange Beck	0	0	0	0	0	5	18	0	0	0	3	0	24	0	14	36
Red Dell Beck	0	0	0	0	0	1	0	0	0	0	0	0	10	46	39	2
Torver Beck	0	0	0	0	0	5	5	0	0	0	2	0	28	26	34	0
Washfall Beck	14	0	0	0	0	6	0	0	36	0	0	0	28	0	16	0
Mill Beck 1	9	0	0	0	0	0	66	9	0	0	16	0	0	0	0	0
Stony Beck	10	0	2	1	6	6	5	0	23	0	0	0	30	0	18	0
Hagg Gill	11	0	0	0	0	0	0	0	27	0	0	0	4	23	34	0
Trout Beck	6	0	0	0	0	3	0	0	16	0	0	0	18	26	30	0
Woundale Beck	7	0	0	0	0	0	0	0	18	0	0	0	2	38	35	0
Hall Gill	4	0	0	0	1	7	6	0	9	0	0	0	35	0	38	0
Chapel Beck	12	0	0	0	0	0	58	12	0	0	19	0	0	0	0	0
Chapel Beck Trib	10	0	0	0	0	0	54	10	0	0	26	0	0	0	0	0
Grayrigg Hall Beck	5	0	0	0	0	12	42	9	0	0	7	23	2	0	0	0
Flodder Beck	8	0	0	0	4	0	39	8	0	0	8	0	32	0	0	0
St Sundays Beck	6	0	0	0	6	0	30	6	0	0	6	0	46	0	0	0
Killington Res Trib	1	0	0	0	10	0	7	1	0	0	1	0	80	0	0	0
River Mint Trib	3	0	0	0	0	0	27	11	0	0	4	54	0	0.5	0.5	0
Borrow Beck	0	0	0	0	0	0	25	0	0.5	0	4	0	0	0.5	70	0
Bannisdale Beck	4	0	0	0	0	0	26	0	9	0	4	0	0	0	57	0
River Sprint	4	0	0	0	0	0	0	0	10	0	0	0	0	26	60	0
Moasdale Beck	0	0	0	0	3	0	0	0	2	0	0	0	12	34	48	0
Castle How Beck	11	0	1	1	5	0	0	0	27	0	0	0	0	32	23	0
Tarn Beck	4	0	0	0	2	0	0	0	9	0	0	0	16	38	30	1
Sling Beck	9	0	0	0	1	0	6	1	19	0	1	0	9	21	34	0
Holehouse Gill	1	0	0	0	2	0	0	0	3	0	0	0	13	17	64	0
Crosby Gill	1	0	0	0	4	0	0	0	2	0	0	0	33	22	38	0
Greendale Gill	7	0	0	0	0	0	0	0	18	0	0	0	0	43	32	0
Nether Beck	4	0	0	0	0	0	0	0	11	0	0	0	0	45	34	6
Whillan Beck	14	0	0	0	0	0	0	0	12	0	0	0	0	32	38	2
Hardknott Gill	12	4	0	0	0	0	0	0	29	0	0	0	0	31	23	0
Whelpside Ghyll	7	0	0	0	0	0	0	0	17	0	0	0	0	31	40	5
Wyth Burn	10	0	0	0	0	0	0	0	26	0	0	0	0	14	50	0
Launchy Ghyll	3	0	0	0	0	0	0	0	7	0	0	0	0	35	55	0
Shoulthwaite Gill	9	0	0	0	0	0	0	0	22	0	0	0	0	32	33	3
Coledale Beck	0	0	0	0	0	12	55	0	0	0	8	0	0	20	5	0
Liza Beck	0	0	0	0	0	18	40	0	0	0	6	0	0	29	7	0
Mill Beck 2	0	0	0	0	0	18	39	0	0	0	6	0	0	29	7	0
Sour Milk Gill	4	4	0	0	0	0	0	0	12	0	0	0	0	45	34	0
Styhead Gill	5	1	0	0	0	0	0	0	14	0	0	0	0	46	34	0
Glenridding Beck	4	0	0	0	0	0	0	0	9	0	0	0	0	19	68	0
Glencoyne Beck	7	0	0	0	0	6	1	1	18	0	0	4	0	15	45	3
Aira Beck	4	0	0	0	0	38	0	0	10	0	0	0	0	4	43	0
Parkhouse Gill	0	0	0	0	0	0	4	4	0	0	0	27	0	30	22	12
Fusedale Beck	6	0	0	0	1	59	0	0	15	0	0	0	8	6	5	0
Heltondale Beck	14	0	0	0	0	17	0	0	35	0	0	0	0	0	34	0
Cawdale Beck	11	0	0	0	0	27	0	0	27	0	0	1	0	0	33	0
Gatescarth Beck	0	0	0	0	0	0	0	0	0	0	0	0	0	35	62	3
Naddle Beck	8	3	0	0	0	0	0	0	20	4	0	7	0	24	28	6
Mosedale Beck	4	0	0	0	0	0	0	0	9	0	0	0	0	14	73	0
Tailbert Gill	4	1	0	0	0	5	0	0	10	1	0	3	28	18	30	0

Table F4 – Deposition loads in the study catchments

(Units are keq ha^{-1} yr^{-1})

Sample	NOx	NHx	TOTS	NMS	TOTBC	NMBC
Rydal Beck	0.958	1.795	3.091	2.289	2.289	0.648
Stock Ghyll	0.901	1.76	2.898	2.163	2.1	0.605
How Beck	0.629	1.008	2.057	1.578	1.435	0.436
Dale Park Beck	0.629	1.008	2.057	1.578	1.435	0.436
Low Cunsey Beck	0.629	1.008	2.057	1.578	1.435	0.436
Belle Grange Beck	0.629	1.008	2.057	1.578	1.435	0.436
Red Dell Beck	0.777	1.362	2.522	1.898	1.819	0.531
Torver Beck	0.629	1.008	2.057	1.578	1.435	0.436
Washfall Beck	0.958	1.795	3.091	2.289	2.289	0.648
Mill Beck 1	0.548	1.038	1.715	1.356	1.103	0.363
Stony Beck	0.781	1.688	2.493	1.899	1.7	0.518
Hagg Gill	0.781	1.688	2.493	1.899	1.7	0.518
Trout Beck	0.781	1.688	2.493	1.899	1.7	0.518
Woundale Beck	0.781	1.688	2.493	1.899	1.7	0.518
Hall Gill	0.781	1.688	2.493	1.899	1.7	0.518
Chapel Beck	0.546	1.032	1.707	1.351	1.091	0.362
Chapel Beck Trib	0.546	1.032	1.707	1.351	1.091	0.362
Grayrigg Hall Beck	0.546	1.032	1.707	1.351	1.091	0.362
Flodder Beck	0.546	1.032	1.707	1.351	1.091	0.362
St Sundays Beck	0.546	1.032	1.707	1.351	1.091	0.362
Killington Res Trib	0.546	1.032	1.707	1.351	1.091	0.362
River Mint Trib	0.758	1.622	2.414	1.844	1.639	0.502
Borrow Beck	0.781	1.688	2.493	1.899	1.7	0.518
Bannisdale Beck	0.781	1.688	2.493	1.899	1.7	0.518
River Sprint	0.781	1.688	2.493	1.899	1.7	0.518
Moasdale Beck	0.958	1.795	3.091	2.289	2.289	0.648
Castle How Beck	0.902	1.661	2.915	2.168	2.144	0.612
Tarn Beck	0.655	1.071	2.14	1.635	1.505	0.854
Sling Beck	0.624	1.001	2.043	1.568	1.424	0.432
Holehouse Gill	0.394	0.675	1.352	1.058	0.907	0.254
Crosby Gill	0.394	0.675	1.352	1.058	0.907	0.254
Greendale Gill	0.534	0.909	1.769	1.338	1.289	0.342
Nether Beck	0.534	0.909	1.769	1.338	1.289	0.342
Whillan Beck	0.602	1.051	1.981	1.49	1.449	0.391
Hardknott Gill	0.958	1.795	3.091	2.289	2.289	0.648
Whelpside Ghyll	0.958	1.795	3.091	2.289	2.289	0.648
Wyth Burn	0.958	1.795	3.091	2.289	2.289	0.648
Launchy Ghyll	0.958	1.795	3.091	2.289	2.289	0.648
Shoulthwaite Gill	0.917	1.722	2.949	2.189	2.179	0.616
Coledale Beck	0.457	0.836	1.381	1.067	0.976	0.262
Liza Beck	0.358	0.525	1.106	0.86	0.787	0.202
Mill Beck 2	0.547	0.936	1.799	1.716	1.312	0.35
Sour Milk Gill	0.958	1.795	3.091	2.289	2.289	0.648
Styhead Gill	0.958	1.795	3.091	2.289	2.289	0.648
Glenridding Beck	0.958	1.795	3.091	2.289	2.289	0.648
Glencoyne Beck	0.958	1.795	3.091	2.289	2.289	0.648
Aira Beck	0.987	1.332	2.19	1.648	1.591	0.444
Parkhouse Gill	0.367	0.672	1.032	0.834	0.671	0.196
Fusedale Beck	0.781	1.688	2.493	1.899	1.7	0.518
Heltondale Beck	0.702	1.495	2.215	1.697	1.504	0.427
Cawdale Beck	0.781	1.688	2.493	1.899	1.7	0.518
Gatescarth Beck	0.781	1.688	2.493	1.899	1.7	0.518
Naddle Beck	0.781	1.688	2.493	1.899	1.7	0.518
Mosedale Beck	0.781	1.688	2.493	1.899	1.7	0.518
Tailbert Gill	0.781	1.688	2.493	1.899	1.7	0.518

F.3 Catchment Characteristics – Abridged details

Table F5 – Catchment Characteristics of the study catchments

Sample	BVG	SKS	SIL	CAR	GR	UPL	FOR	AGR	DEP1	DEP2	DEP3	DEP4	DEP5	DEP6	DEP7	THP	THI	GLY	PTY
Rydal Beck	100	0	0	0	0	99	1	0	0	0	0	0	0	0	100	10	26	0	64
Stock Ghyll	100	0	0	0	0	97	0	3	0	0	0	0	0	0	100	4	10	0	86
How Beck	0	0	100	0	0	0	23	77	0	0	0	0	100	0	0	24	8	0	67
Dale Park Beck	0	0	100	0	0	0	100	0	0	0	0	0	100	0	0	28	6	0	66
Low Cunsey Beck	0	0	100	0	0	0	94	6	0	0	0	0	100	0	0	22	8	0	70
Belle Grange Beck	0	0	100	0	0	0	83	14	0	0	0	0	100	0	0	18	3	0	79
Red Dell Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	0	0	0.5	99.5
Torver Beck	59	0	41	0	0	91	0	9	0	0	0	0	100	0	0	5	2	0.5	92.5
Washfall Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	0	100	14	36	0	50
Mill Beck 1	0	0	100	0	0	0	0	100	0	0	100	0	0	0	0	75	25	0	0
Stony Beck	100	0	0	0	0	81	0	19	0	0	0	0	0	100	0	15	25	7	54
Hagg Gill	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	10.4	27.1	0.3	61.2
Trout Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	7	18	0	75
Woundale Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	6	16.2	0.8	77
Hall Gill	59	0	0	41	0	99.8	0	0.2	0	0	0	0	0	100	0	10	9.6	1.2	79.2
Chapel Beck	0	0	100	0	0	0	0	100	0	0	100	0	0	0	0	70	31	0	0
Chapel Beck Trib	0	0	100	0	0	0	0	100	0	0	100	0	0	0	0	64	36	0	0
Grayrigg Hall Beck	0	0	88	12	0	15	0	85	0	0	100	0	0	0	0	47	16	23	14
Flodder Beck	0	0	100	0	0	37	0	63	0	0	100	0	0	0	0	47	16	4	32
St Sundays Beck	0	0	100	0	0	35	0	65	0	0	100	0	0	0	0	36	12	6	46
Killington Res Trib	0	0	100	0	0	40	0	60	0	0	100	0	0	0	0	8	2	10	80
River Mint Trib	0	0	100	0	0	82	0	18	0	0	0	0	0	100	0	30	15	54	1
Borrow Beck	2	0	74	24	0	100	0	0	0	0	0	0	0	100	0	25.1	4.2	0	70.7
Bannisdale Beck	0	0	60	40	0	100	0	0	0	0	0	0	0	100	0	30	13	0	57
River Sprint	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	4	10	0	86
Moasdale Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	0	100	0.5	2.3	3.2	94
Castle How Beck	100	0	0	0	0	78.5	21.5	0	0	0	0	0	0	0	100	11	28	6	55
Tarn Beck	100	0	0	0	0	100	0	0	0	0	0	0	100	0	0	4.4	9.2	2	84.4
Sling Beck	100	0	0	0	0	97	0	3	0	0	0	0	100	0	0	15	21	1	64
Holehouse Gill	100	0	0	0	0	100	0	0	0	100	0	0	0	0	0	1	3	2	94
Crosby Gill	100	0	0	0	0	100	0	0	0	100	0	0	0	0	0	1	2	4	93
Greendale Gill	46	0	0	0	55	100	0	0	0	0	0	100	0	0	0	7	18	0	75
Nether Beck	73	0	0	0	28	99	0	0	0	0	0	100	0	0	0	4	11	0	85
Whillan Beck	63	0	0	0	38	100	0	0	0	0	0	0	100	0	0	14.5	12	0	73.5
Hardknott Gill	100	0	0	0	0	100	0	0	0	0	0	0	0	0	100	16	29.1	0.3	54.6
Whelpside Ghyll	100	0	0	0	0	95	0	0	0	0	0	0	0	0	100	7	17	0	76
Wyth Burn	100	0	0	0	0	100	0	0	0	0	0	0	0	0	100	10	26	0	64
Launchy Ghyll	100	0	0	0	0	100	0	0	0	0	0	0	0	0	100	3	7	0	90
Shoulthwaite Gill	100	0	0	0	0	93	8	0	0	0	0	0	0	0	100	9.3	22.3	0.4	68
Coledale Beck	0	100	0	0	0	99	1	0	0	100	0	0	0	0	0	55	8	0	37
Liza Beck	0	100	0	0	0	100	0	0	100	0	0	0	0	0	0	40	6.5	0	53.5
Mill Beck 2	0	100	0	0	0	100	0	0	0	0	0	100	0	0	0	39	6	0	55
Sour Milk Gill	91	0	0	0	10	100	0	0	0	0	0	0	0	0	100	8	12	0	79
Styhead Gill	99	0	0	0	1	100	0	0	0	0	0	0	0	0	100	5.5	14	0	80.5
Glenridding Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	0	100	4	9	0.1	86.9
Glencoyne Beck	99	1	0	0	0	100	0	0	0	0	0	0	0	0	100	8	19	4	69
Aira Beck	100	0	0	0	0	100	0	0	0	0	0	0	100	0	0	4	10	0	85
Parkhouse Gill	50	50	0	0	0	62	0	35	100	0	0	0	0	0	0	4.4	4.6	27	64
Fusedale Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	14	35	0	51
Heltondale Beck	100	0	0	0	0	55	0	45	0	0	0	0	0	100	0	6	15	1	78
Cawdale Beck	100	0	0	0	0	76	0	24	0	0	0	0	0	100	0	11.4	27.4	1	60.2
Gatescarth Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	0	0	0	100
Naddle Beck	74	0	0	0	26	99	0	0.5	0	0	0	0	0	100	0	11	24	7	58
Mosedale Beck	100	0	0	0	0	100	0	0	0	0	0	0	0	100	0	4	9	0	87
Tailbert Gill	100	0	0	0	0	88	0	12	0	0	0	0	0	100	0	5	11	3	81

APPENDIX G

Modelling Results

G.1 Calibration of the MAGIC model to the Lake District data

The MAGIC model requires data for surfacewater chemistry, rainfall chemistry and volume, soil chemistry and other soil characteristics for calibration and subsequent application. Calibration of MAGIC occurred at 47 of the 55 survey sites.

G.1.1. Surfacewater chemistry

The streamwater chemistry was monitored over the period, May 1996 to March 1997 inclusive, by six synoptic surveys. The chemistry of the sites represents the different geological, soil, land use and acid deposition combinations. The streamwater chemistry is fully discussed elsewhere in the thesis (Section 4.3).

G.1.2. Rainfall, Runoff and Evapotranspiration

MAGIC is a flux based model and requires specification of the annual water budget at each site in terms of rainfall, runoff and evapotranspiration (Jenkins *et al.*, 1997). The program, TSTCD, used during the GIS aspect of the project provided estimates of rainfall, runoff and potential evapotranspiration (Section 4.2). Evapotranspiration ranges from 10% for a moorland catchment (Robson *et al.*, 1991) to 25% for a forested catchment (Paul Whitehead, University of Reading, personal communication). The reliability of the TSTCD data was assessed and required no recalculation since all values fell within the deemed range. The data used for each site can be found in Appendix G.2.1 (Table G2).

G.1.3. Deposition chemistry

Wet deposition of all major ions is measured at 32 sites across the UK as part of the Acid Deposition Monitoring Network (ADMN) administered by AEA Technology. The most suitable deposition collector for the survey based on proximity is Bannisdale (NY 515043), which has been sampled weekly since 1986. The Bannisdale rainfall collector is approximately 50km from the sea and at an altitude of 265m. The Lake District is a maritime region and experiences a high sea-salt influence in precipitation. The rainfall chemistry of the Lake District is characterised by concentrations of sulphate and nitrate in excess of sea-salt influence indicating a considerable anthropogenic input. However, the

rainfall collector is in the east of the study region and may not be representative of the whole study area, especially catchments proximal to the sea. In addition, rainfall chemistry has been shown to be highly variable with altitude (Fowler *et al.*, 1988; Dore *et al.*, 1992). Much of the rainfall in the uplands of western Britain arises through orographic enhancement of precipitation by the seeder-feeder scavenging process (Choularton *et al.*, 1988). Since the rainfall collector is at an altitude of 265m, there could be significant differences in the rainfall composition at the higher sites. For this reason the rainfall data from Bannisdale was recalculated based on the assumption that chloride is conservative. This is probably a valid assumption, as the Lake District sites don't possess a catchment source of chloride.

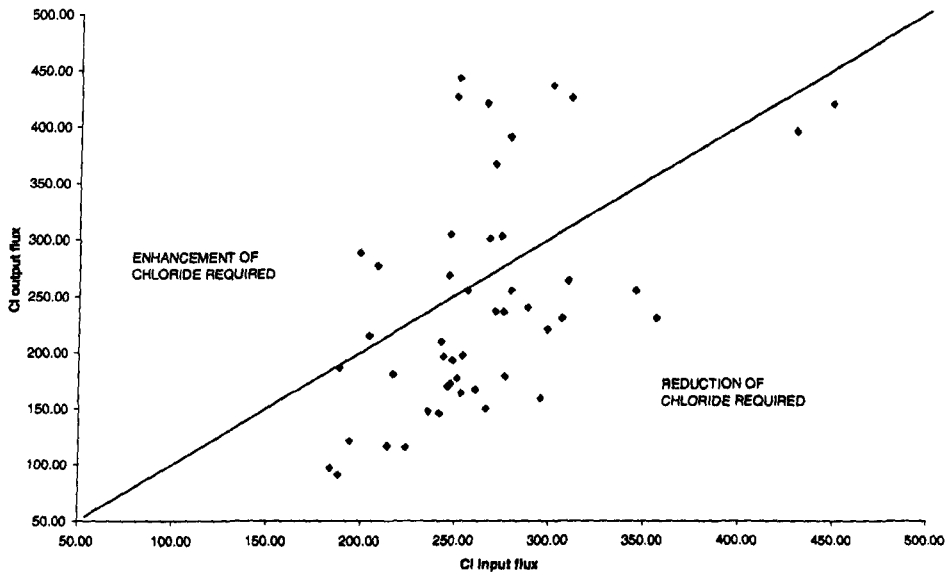
MAGIC is based on the principals of ion-balance and thus correct simulation of conservative ions is important to the accuracy of model predictions for non-conservative ions (Jenkins *et al.*, 1997). The enhancement/reduction required to the chloride input flux was calculated using the following formula:

$$Cl_{dep} * AP = Cl_{str} * AR$$

where Cl_{dep} is the total deposition concentration of chloride (wet, dry and occult);
AP is the annual volume of precipitation in metres;
Cl_{str} is the measured concentration in streamwater; and
AR is the annual runoff in metres.

The Bannisdale rainfall data gives a good approximation of the input fluxes of chloride required. However, at all but two sites some enhancement or reduction of the inputs was necessary to balance the output flux of chloride (Figure G1).

Figure G1 - Input-output budgets for chloride from the Bannisdale raingauge (input flux) and the streamwater chemistry of 47 Lake District sites (output flux)



The enhancement / reduction of chloride input is assumed to be sea-salt driven in that sites nearer the sea would be expected to have higher chloride in precipitation than sites farther away (This is in general agreement with the location of the sites). In order to maintain the pH of the rainfall, base cations and sulphate are also added / removed in the appropriate sea-salt ratio. The deposition concentrations were recalculated using the following formula:

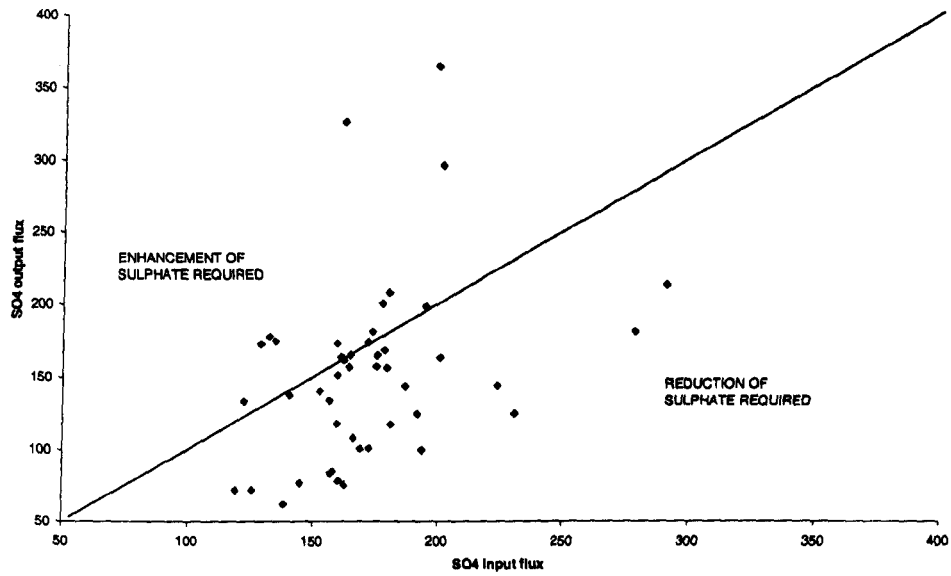
$$BC_{dep} = BC_{wet} + (f_{ss} * Cl_{er})$$

where BC_{dep} is total deposition of base cations (wet, dry and occult);
BC_{wet} is the observed wet deposition concentration;
f_{ss} is the sea-salt fraction (where Na^+=0.86, Ca^{2+}=0.04, Mg^{2+}=0.21, K^+=0.019 and SO_4^{2-}=0.104);
Cl_{er} is the change in chloride calculated from the input-output mass balance.

The soils in the Lake District are relatively young and therefore have little capacity for sulphate absorption (Barlow, 1994). This suggests that sulphate adsorption value of the model should be set relatively low. Sulphate in this respect is steady state (i.e. output balancing input), and this pseudo-conservative behaviour allows the enhancement / reduction to occur in the same way as chloride. The discrepancy in sulphate flux is assumed to be dry deposition and can be apportioned to SO_2 and SO_4 aerosols. In general, the Bannisdale rainfall data gives a good approximation of the input fluxes of 'wet' sulphate required. However, at all but four sites some enhancement or reduction of the inputs was

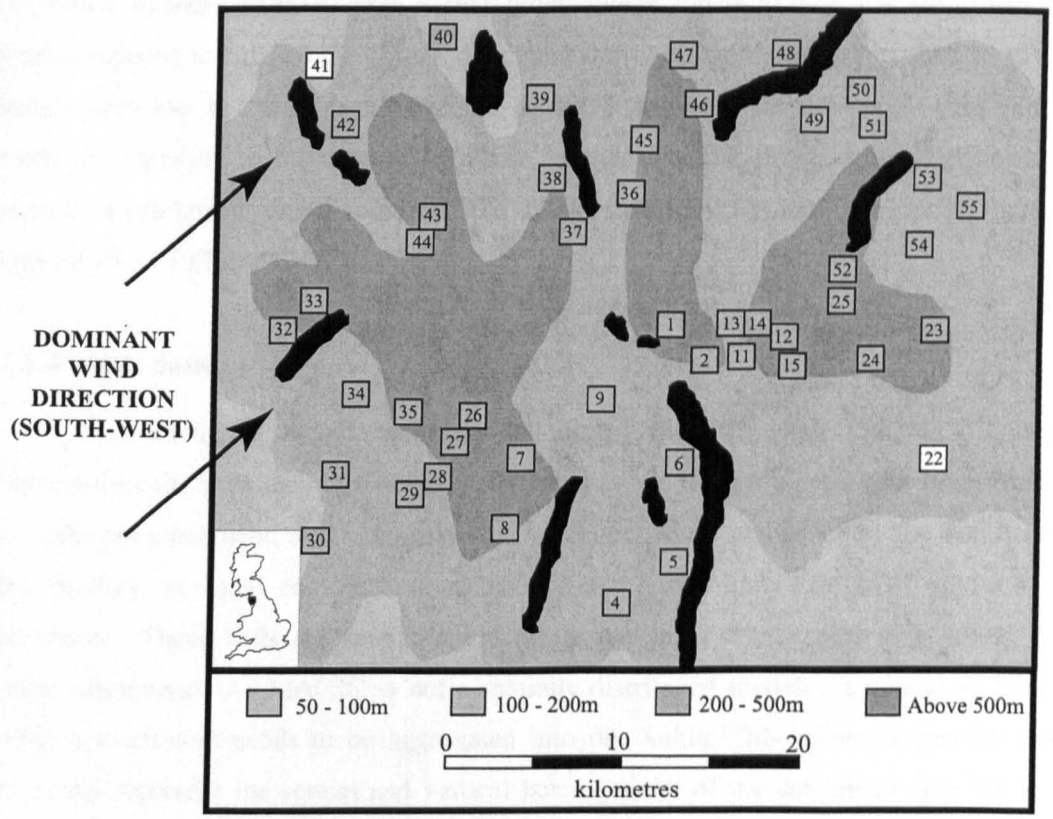
necessary to balance the output flux of sulphate (Figure G2). The deposition data used for each site can be found in Appendix G.2.1 (Table G3).

Figure G2 - Input-output budgets for sulphate from the Bannisdale raingauge (input flux) and the water chemistry of 47 Lake District streams (output flux)



Using a map of the study area showing relief and dominant wind direction, the enhancement / removal of ions shows some interesting patterns (Figure G3). The distribution of sites requiring addition of chloride and the other ions, display three patterns. The first pattern, relates to sites 26, 27, 32, 33, 34 and 35, which are located on the windward side of the high ground suggesting an orographic influence (cf. Fowler *et al.*, 1988). The second pattern, relates to sites 4, 5, 6 and 36, which have some forestry suggesting that scavenging of airborne particulates by the trees has occurred (cf. Neal *et al.*, 1992c). The third pattern, relates to sites 39, 40 and 42, which are located in the relief range 200 to 500m but have no higher ground between themselves and the sea along the dominant wind gradient.

Figure G3 - Map showing the sites used in the MAGIC application. Also showing enhancement of ions (pink), removal of ions (blue), relief and dominant wind direction.



The distribution of sites requiring removal of chloride and the other ions, also display three patterns. The first pattern, relates to sites 7, 8, 9, 37, 38, 43 and 44, which are located on the leeward side of high ground suggesting a rain shadow effect. A similar explanation can be given for the second pattern, relating to sites 1, 2, 11-15, 23, 25 and 45-55, which are located on the leeward side of the large amount of high ground in the west of the study area. The third pattern, relates to sites 28, 29, 30 and 31, which are located on the plateau prior to the high ground in the west of the study site.

This suggests that the 20 x 20km scale used for the atmospheric deposition map (Section 4.2.1d) is inaccurate for catchment scale modelling. The enhancements of deposition utilise the mean altitude and forest cover of a grid square to estimate depositional differences. These are calculated from the 32 wet deposition monitoring sites using the geostatistical technique of kriging (UKRGAR, 1997). Therefore, the mean characteristics of a 20 x 20km square may poorly reflect the altitude and forest cover of an individual site and lead to an over or underestimation of atmospheric deposition. It is unsurprising given this fact that the atmospheric deposition used in the MAGIC model varies considerably from the mapped data (Section 4.2.1d).

MAGIC represents nitrate and ammonium in an extremely simplified manner. The catchment retains the nitrate and ammonium deposition to certain degree (i.e. usually by vegetation uptake). MAGIC uses a first order uptake function, which is the percentage uptake required to balance the observed streamwater concentrations. Ammonium levels are usually very low in Lake District streams, so 100% uptake is assumed at all sites. Nitrate levels are variable, so the amount of nitrate leached into the streamwater determines the amount of catchment uptake required. The uptake data used for each site can be found in Appendix G.2.1 (Table G4).

G.1.4 Soils data

The catchment boundaries generated during the GIS work (Section 4.2) were overlaid over the soils map of Great Britain (Jarvis *et al.*, 1984a) to define the proportion of soil units per catchment. Soil chemistry data was supplied under licence by the Soil Survey (Ian Bradley, personal communication) for the seven soil units that exist in the study catchments. These soils are spatially variable across the Lake District as a whole, and within catchments. As MAGIC is not a spatially distributed model, the spatial variability within a catchment needs to be aggregated into one value. This value (or profile) must accurately represent the spatial and vertical heterogeneity of the catchment. The soil data provided by the Soil Survey was an average for a number of profiles, also averaged over depth. The catchment value is obtained by weighting the physical and chemical characteristics by the proportion of the soil unit in the catchment using the following formula:

$$X_{catch} = \Sigma (X_i * f_i)$$

where X_{catch} is the catchment weighted soil value;
X_i is the lumped parameter of the *i*th soil characteristic; and
f_i is the *i*th soil unit (proportion of the catchment).

This process generates one value for each parameter that is both depth and spatially weighted across the catchment for input into MAGIC. The soils data used for each site can be found in Appendix G.2.1 (Table G5).

G.1.5 Optimisation of base cations

This procedure involved the use of MAGIC coupled to an optimisation routine and was used to estimate weathering rates and background base saturation levels for the Lake

District data. The optimisation routine is based on the Rosenbrock algorithm and uses a 140 year hindcast simulation (1856-1996).

The soil and water characteristics measured in the field are considered "fixed" parameters in the model. These target variables consist of the surfacewater cation concentrations and the soil exchangeable cation concentrations. The uncertainty in the measurement of fixed parameters (i.e. analytical and sampling errors), and the lumping of soil data suggests that a "fuzzy" optimisation procedure is required for calibration. In fuzzy calibration, the target variables have a range of acceptable values (or a "window"). The size of the windows is based on known measurement errors. The windows are usually set as ± 5μeq l^{-1} or 10% for surfacewater concentrations and ± 0.5 or 10% for soil base cations, whichever the greatest of the two conditions. All values must be reproduced within this window if calibration is to be successful. The "windows" for each site can be found in Appendix G.2.2. Base-cation weathering rates and soil base cation selectivity coefficients are not directly measurable and are considered adjustable model parameters. These are the parameters that require optimisation in the calibration procedure.

The fuzzy procedure consists of multiple calibrations, based on the Rosenbrock algorithm, until the minimum error fit to the target variables is achieved. The optimisation algorithm is stopped and the calibration considered complete when the simulated values are within the pre-specified windows of the target variables. This procedure was undertaken ten times at each site. By analysing the optimisation output, maximum and minimum uncertainty limits and the average of all the successful calibrations can be found. The output from the optimisation procedure for each site can be found in Appendix G.2.3.

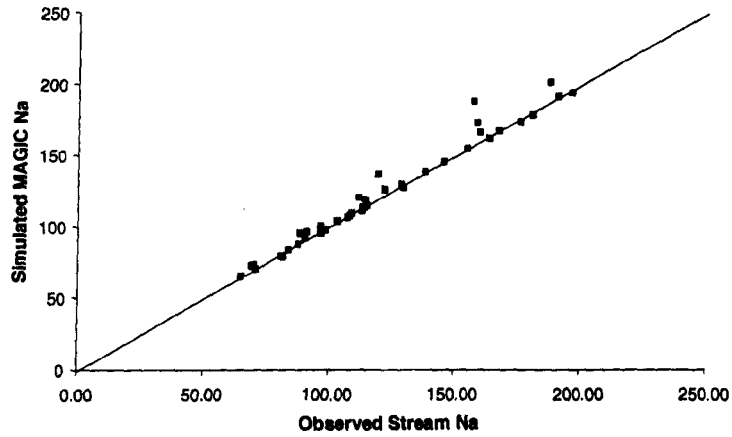
G.1.6 Examination of Lake District data after the MAGIC calibration

The catchment data for each site was calibrated in the following order: 1) Chloride and sulphate concentrations in precipitation were adjusted using the sea-salt and dry deposition corrections (Appendix G.1.3); 2) Nitrate and ammonium concentrations in precipitation were calibrated to match observed surfacewater chemistry output using the first-order uptake function (Appendix G.1.3); 3) Base cations in the streamwater were fitted using an optimisation procedure (Appendix G.1.5).

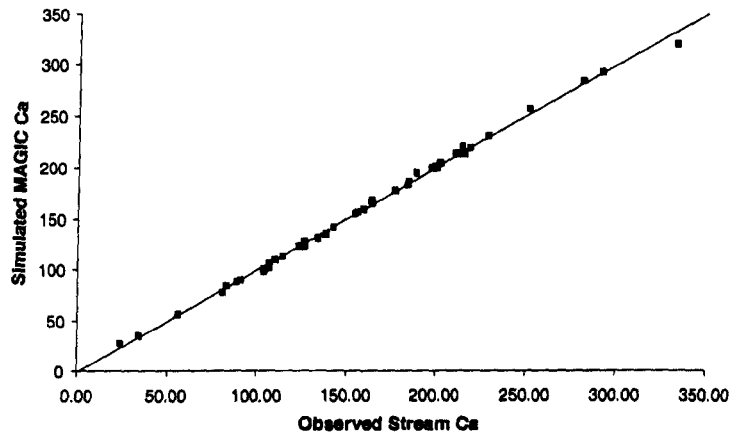
The model was successfully calibrated to the forty-seven sites with simulated chemistry of surfacewater concentrations in good agreement with observed concentrations for all cations (Figures G4 and G5). The simulated sodium falls within the 10% window but several sites are away from the 1:1 line (Figure G4a). Sites 2, 4, 5, 39, 40 and 42 have simulated sodium above the observed concentrations. These sites have a sodium / chloride

ratio below that of seasalt (i.e. 0.86), which probably accounts for the overestimated concentrations. The simulated calcium falls almost on the 1:1 line for all sites, suggesting a good calibrated fit (Figure G4b).

Figure G4 - Comparison of MAGIC simulated and present day observed chemistry for a) Na^+ and b) Ca^{2+} (Units are μeq l-1)



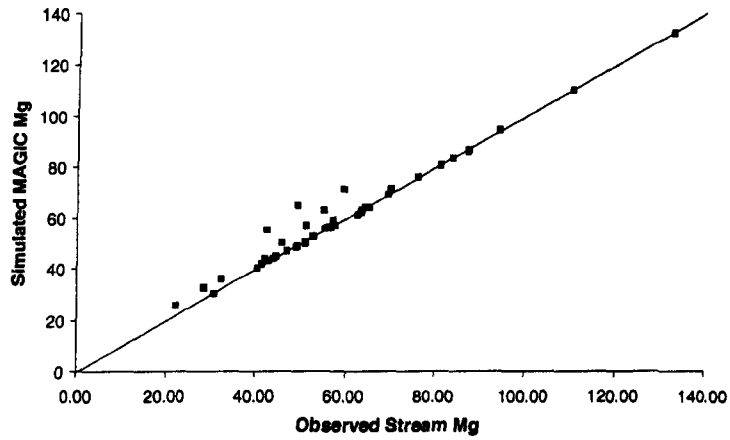
a.



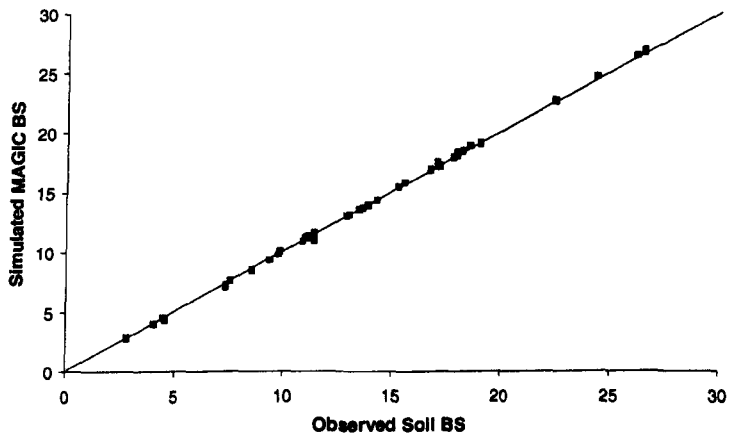
b.

The simulated magnesium falls within the 10% window but several sites are away from the 1:1 line (Figure G5a). Sites 2, 4, 6, 35, 36 and 39 have simulated magnesium above the observed concentrations. The overestimation of magnesium concentrations is probably due to the fact that MAGIC works on the principles of ion balance and requires electroneutrality of streamwater. The simulated base saturation falls almost on the 1:1 line for all sites, suggesting a good calibrated fit (Figure G5b).

Figure G5 - Comparison of MAGIC simulated and present day observed chemistry for a) Mg^{2+} and b) Soil base saturation
(Units are $\mu eq\ l^{-1}$ for stream variable and % of CEC for base saturation)



a.



b.

The calibration procedure uses a historical simulation of acid deposition over 140 years (Table G1 and Figure G6) which can be used to predict the acidification of soils and streamwater over time. The simulation shows the trend of acid deposition over the last 140 years. This has been estimated to reflect the patterns of (i) Early industrial growth in the late 1850s; (ii) "Tall stacks" policies after the Clean Air Acts in the 1950s and 1960s; (iii) Peak emissions in the late 1970s; and (iv) Emissions curtailment following international agreements in the late 1980s and 1990s (Warren-Spring-Laboratory, 1987).

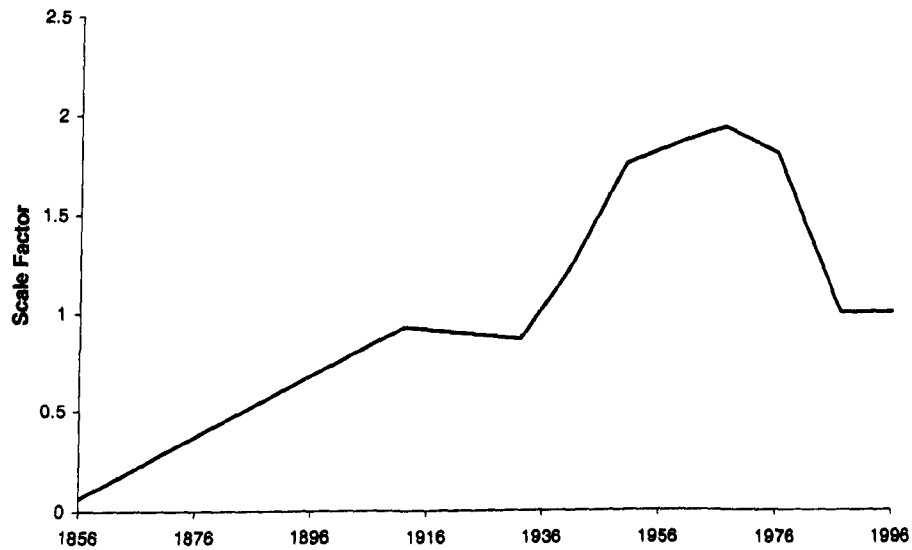
Table G1 - Estimated historical acid deposition trends used in the calibration procedure

1856 = Scale 0.00 1996 = Scale 1.00

Sequence of changes in Hindcast deposition

Break	Year	Scale Factor
1	1856	0.060
2	1912	0.930
3	1932	0.870
4	1940	1.200
5	1950	1.750
6	1961	1.870
7	1967	1.930
8	1976	1.800
9	1987	1.000

Figure G6 - Estimated historical trends of acid deposition relative to present day deposition flux (i.e. scale factor of 1.0).



G.2 MAGIC data from optimisation procedure

G.2.1 Individual site data entered into the model prior to optimisation procedure

Data such as rainfall and runoff (Table G2), deposition chemistry (Table G3), nitrate and ammonia uptake (Table G4) and soil parameters like depth, bulk density and base saturation (Table G5) are all entered into the model on a site-specific basis. This section gives details of the raw data for these parameters from each individual site.

Table G2 - Rainfall and runoff data for each individual site used in the MAGIC calibration procedure (Data derived using TSTCD program. Units are mm yr^{-1}).

Sample	Rainfall	Runoff
Rydal Beck	2435	2034
Stock Ghyll	2250	1828
Dale Park Beck	1869	1417
Low Cunsey Beck	1787	1331
Belle Grange Beck	1834	1382
Red Dell Beck	2754	2310
Torver Beck	2284	1837
Washfall Beck	2213	1765
Stony Beck	2172	2172
Hagg Gill	2235	1825
Trout Beck	2394	1992
Woundale Beck	2256	1842
Hall Gill	2118	1692
River Mint Trib	1697	1293
Borrow Beck	2212	1811
Bannisdale Beck	2277	1875
River Sprint	2487	2089
Moasdale Beck	3104	2684
Castle How Beck	2499	2069
Tarn Beck	2591	2151
Sling Beck	2225	1786
Holehouse Gill	2179	1738
Crosby Gill	2192	1750
Greendale Gill	2386	1945
Nether Beck	2700	2312
Whillan Beck	2430	1999
Hardknott Gill	2462	2032
Whelpside Ghyll	2788	2490
Wyth Burn	3202	3202
Launchy Ghyll	2687	2380
Shoulthwaite Gill	2218	1902
Coledale Beck	2242	1921
Liza Beck	2304	1974
Mill Beck 2	2407	2106
Sour Milk Gill	3864	3571
Styhead Gill	4035	3725
Glenridding Beck	2782	2464
Glencoyne Beck	2475	2096
Aira Beck	2510	2128
Parkhouse Gill	1652	1250
Fusedale Beck	2011	1614
Heltondale Beck	1693	1290
Cawdale Beck	1925	1524
Gatescarth Beck	2659	2261
Naddle Beck	1951	1549
Mosedale Beck	2346	1948
Tailbert Gill	1744	1343

Table G3 - MAGIC present-day (1996) deposition for each individual site after base cation, chloride and sulphate reduction / enhancement
(Data derived using equations in Appendix G.1.3. Units are meq m^{-2} yr^{-1})

Sample	Ca	Mg	Na	K	NH4	Cl	SO4	NO3
Rydal Beck	24.4	25.0	83.4	3.7	49.9	97.2	70.6	35.2
Stock Ghyll	28.4	46.0	169.4	5.6	49.9	197.3	81.0	35.2
Dale Park Beck	26.5	35.8	127.5	4.7	49.9	148.5	75.9	35.2
Low Cunsey Beck	27.0	38.4	138.5	5.0	49.9	161.3	77.2	35.2
Belle Grange Beck	25.3	29.3	100.9	4.1	49.9	117.6	72.7	35.2
Red Dell Beck	23.9	22.2	71.9	3.5	49.9	83.8	69.2	35.2
Torver Beck	24.0	22.7	74.1	3.5	49.9	86.4	69.4	35.2
Washfall Beck	23.6	20.7	65.8	3.3	49.9	76.8	68.4	35.2
Stony Beck	23.2	18.6	57.4	3.2	49.9	67.0	67.4	35.2
Hagg Gill	24.0	22.7	74.2	3.5	49.9	86.5	69.4	35.2
Trout Beck	23.1	17.7	53.7	3.1	49.9	62.7	67.0	35.2
Woundale Beck	23.7	21.1	67.4	3.4	49.9	78.7	68.6	35.2
Hall Gill	23.3	19.2	59.6	3.2	49.9	69.6	67.7	35.2
River Mint Trib	25.0	27.7	94.5	4.0	49.9	110.1	71.9	35.2
Borrow Beck	25.4	30.1	104.2	4.2	49.9	121.5	73.1	35.2
Bannisdale Beck	23.4	19.7	61.8	3.3	49.9	72.2	68.0	35.2
River Sprint	23.4	19.7	61.8	3.3	49.9	72.1	67.9	35.2
Moasdale Beck	23.8	21.8	70.5	3.5	49.9	82.2	69.0	35.2
Castle How Beck	26.8	37.5	134.5	4.9	49.9	156.7	76.7	35.2
Tarn Beck	24.3	24.0	79.5	3.7	49.9	92.7	70.1	35.2
Sling Beck	23.7	20.9	66.5	3.4	49.9	77.6	68.5	35.2
Holehouse Gill	24.4	24.8	82.6	3.7	49.9	96.3	70.5	35.2
Crosby Gill	24.1	23.4	77.0	3.6	49.9	89.8	69.8	35.2
Greendale Gill	27.6	41.7	151.7	5.2	49.9	176.7	78.8	35.2
Nether Beck	27.0	38.6	139.0	5.0	49.9	161.9	77.3	35.2
Whillan Beck	26.6	36.3	129.6	4.8	49.9	151.0	76.2	35.2
Hardknott Gill	25.5	30.4	105.7	4.2	49.9	123.2	73.3	35.2
Whelpside Ghyll	26.7	36.7	131.2	4.8	49.9	152.9	76.3	35.2
Wyth Burn	23.4	19.7	61.7	3.3	49.9	72.0	67.9	35.2
Launchy Ghyll	23.8	21.8	70.4	3.4	49.9	82.1	69.0	35.2
Shoulthwaite Gill	26.1	33.4	118.0	4.5	49.9	137.5	74.7	35.2
Coledale Beck	28.2	44.6	163.7	5.5	49.9	190.6	80.3	35.2
Liza Beck	25.0	27.8	94.9	4.0	49.9	110.6	71.9	35.2
Mill Beck 2	25.6	30.8	107.2	4.3	49.9	125.0	73.4	35.2
Sour Milk Gill	24.7	26.1	88.1	3.8	49.9	102.7	71.1	35.2
Styhead Gill	24.7	26.5	89.4	3.9	49.9	104.3	71.3	35.2
Glenridding Beck	24.4	24.5	81.4	3.7	49.9	95.0	70.3	35.2
Glencoyne Beck	24.4	24.6	81.8	3.7	49.9	95.4	70.4	35.2
Aira Beck	24.6	25.9	87.2	3.8	49.9	101.6	71.0	35.2
Parkhouse Gill	22.9	16.9	50.4	3.0	49.9	58.9	66.6	35.2
Fusedale Beck	22.9	16.6	49.1	3.0	49.9	57.4	66.4	35.2
Heltondale Beck	22.7	15.9	46.1	2.9	49.9	53.9	66.1	35.2
Cawdale Beck	23.0	17.3	52.0	3.0	49.9	60.7	66.8	35.2
Gatescarth Beck	23.0	17.2	51.3	3.0	49.9	60.0	66.7	35.2
Naddle Beck	24.3	24.1	79.7	3.7	49.9	92.9	70.1	35.2
Mosedale Beck	23.4	19.5	61.0	3.2	49.9	71.2	67.8	35.2
Tailbert Gill	23.3	19.2	59.7	3.2	49.9	69.7	67.7	35.2

Table G4 - Percentage NO_3^- and NH_4^+ uptake in the soil aspect of the MAGIC model required to balance surfacewater concentrations at the individual sites

Sample	NO_3 uptake	NH_4 uptake
Rydal Beck	71.5	100
Stock Ghyll	43	100
Dale Park Beck	28	100
Low Cunsey Beck	28	100
Belle Grange Beck	82	100
Red Dell Beck	32.5	100
Torver Beck	62	100
Washfall Beck	91	100
Stony Beck	28	100
Hagg Gill	60	100
Trout Beck	78	100
Woundale Beck	92	100
Hall Gill	82	100
River Mint Trib	77	100
Borrow Beck	99	100
Bannisdale Beck	94.5	100
River Sprint	55	100
Moasdale Beck	72	100
Castle How Beck	22	100
Tarn Beck	28	100
Sling Beck	99	100
Holehouse Gill	100	100
Crosby Gill	86	100
Greendale Gill	67	100
Nether Beck	70	100
Whillan Beck	82	100
Hardknott Gill	76	100
Whelpside Ghyll	30	100
Wyth Burn	88	100
Launchy Ghyll	97	100
Shoulthwaite Gill	92	100
Coledale Beck	96	100
Liza Beck	85	100
Mill Beck 2	100	100
Sour Milk Gill	74	100
Styhead Gill	43	100
Glenridding Beck	70	100
Glencoyne Beck	90	100
Aira Beck	100	100
Parkhouse Gill	84	100
Fusedale Beck	100	100
Heltondale Beck	100	100
Cawdale Beck	96	100
Gatescarth Beck	77	100
Naddle Beck	92	100
Mosedale Beck	98	100
Tailbert Gill	98	100

Table G5 - Soil depth, bulk density, cation exchange capacity (CEC), exchangeable base cations (Ca, Mg, Na, K) and base saturation used at each site.
(Units are m – soil depth, kg m^{-3} – bulk density, meq m^{-3} – CEC, % of CEC – exchangeable base cations, and % of exchangeable base cations added together – base saturation)

Sample	Soil Depth	Bulk Density	CEC	Ca	Mg	Na	K	BS
Rydal Beck	0.3	706	392	7.3	5.9	0.3	0.8	14.3
Stock Ghyll	1.3	1202	186	3.5	2.5	0.6	0.7	7.4
Dale Park Beck	1.1	1222	144	8.3	6.2	0.4	0.7	15.5
Low Cunsey Beck	1.3	1301	130	7.5	1.9	0.8	0.8	11.1
Belle Grange Beck	1.4	1288	145	3.6	2.6	0.6	0.7	7.6
Red Dell Beck	0.1	450	558	0.5	0.9	0.9	0.5	2.8
Torver Beck	1.2	1138	228	1.8	1.3	0.7	0.7	4.5
Washfall Beck	1.2	1244	144	6.7	5.0	0.5	0.7	12.9
Stony Beck	1.1	1200	144	9.8	7.4	0.4	0.7	18.2
Hagg Gill	0.7	955	216	14.8	10.9	0.1	0.7	26.5
Trout Beck	0.3	665	408	7.2	5.6	0.3	0.8	13.9
Woundale Beck	0.8	922	310	4.5	3.6	0.5	0.8	9.4
Hall Gill	1.4	1017	222	7.7	4.9	0.4	0.5	13.5
River Mint Trib	0.1	450	558	0.5	0.9	0.9	0.5	2.8
Borrow Beck	1.1	598	331	16.1	10.2	0.0	0.3	26.5
Bannisdale Beck	1.3	519	469	10.9	6.0	0.1	0.1	17.0
River Sprint	0.8	506	434	9.7	6.3	0.2	0.5	16.7
Moasdale Beck	0.8	464	476	6.5	3.8	0.3	0.5	11.2
Castle How Beck	0.4	770	351	9.0	7.1	0.3	0.8	17.2
Tarn Beck	0.3	611	475	1.6	1.6	0.5	0.9	4.6
Sling Beck	0.7	796	341	7.4	5.4	0.4	0.7	13.9
Holehouse Gill	1.1	428	456	9.4	5.3	0.2	0.4	15.3
Crosby Gill	1.1	740	362	5.5	3.3	0.4	0.6	9.8
Greendale Gill	1.0	1194	152	11.2	5.4	0.6	0.8	18.0
Nether Beck	0.2	578	475	3.9	3.4	0.4	0.9	8.5
Whillan Beck	0.8	506	434	9.7	6.3	0.2	0.5	16.7
Hardknott Gill	0.3	642	434	5.6	4.6	0.4	0.8	11.4
Whelpside Ghyll	0.7	597	382	10.9	7.4	0.2	0.5	19.0
Wyth Burn	0.9	634	351	13.1	8.7	0.1	0.5	22.5
Launchy Ghyll	0.3	455	522	3.5	2.6	0.4	0.8	7.3
Shoulthwaite Gill	0.5	720	361	9.6	7.2	0.2	0.7	17.8
Coledale Beck	0.5	930	247	13.3	10.2	0.1	0.8	24.3
Liza Beck	0.2	578	475	3.9	3.4	0.4	0.9	8.5
Mill Beck 2	0.4	770	351	9.0	7.1	0.3	0.8	17.2
Sour Milk Gill	0.1	482	537	1.4	1.5	0.5	0.9	4.2
Styhead Gill	0.2	578	475	3.9	3.4	0.4	0.9	8.5
Glenridding Beck	1.1	356	466	11.6	6.6	0.1	0.3	18.5
Glencoyne Beck	0.8	393	504	7.8	4.5	0.3	0.4	13.0
Aira Beck	1.0	736	485	6.6	3.8	0.3	0.2	10.9
Parkhouse Gill	0.9	966	310	1.5	1.2	0.6	0.8	4.1
Fusedale Beck	0.9	845	273	15.1	10.5	0.1	0.5	26.1
Heltondale Beck	0.7	1065	413	5.1	4.1	0.3	0.4	9.8
Cawdale Beck	1.0	764	339	13.2	8.8	0.1	0.3	22.4
Gatescarth Beck	0.7	378	517	6.3	3.8	0.3	0.6	11.0
Naddle Beck	0.6	419	502	6.5	4.0	0.3	0.6	11.4
Mosedale Beck	1.0	406	455	11.0	6.5	0.2	0.4	17.9
Tailbert Gill	0.1	450	558	0.5	0.9	0.9	0.5	2.8

G.2.2 The 'windows' used for each site during the optimisation procedure

Data such as streamwater base cations (Table G6) and soil exchangeable base cations (Table G7) are considered target variables by the model. The target variables must be reproduced within an acceptable window to optimise the annual weathering rate and initial (i.e. 1856) base saturation of each site. This section gives details of the target 'windows' from each individual site.

Table G6 - The measured surfacewater base cation concentrations and the target 'windows' for each site. (Units are ueq l^{-1})

Sample	Ca	Ca window	Mg	Mg window	Na	Na window	K	K window
Rydal Beck	142	(128 - 156)	53	(47 - 58)	97	(87 - 106)	1	(0 - 6)
Stock Ghyll	215	(194 - 237)	55	(49 - 60)	188	(169 - 206)	4	(0 - 9)
Dale Park Beck	228	(205 - 251)	59	(53 - 65)	160	(144 - 176)	5	(0 - 10)
Low Cunsey Beck	333	(300 - 366)	70	(63 - 77)	159	(143 - 174)	7	(2 - 12)
Belle Grange Beck	214	(192 - 235)	51	(46 - 56)	138	(124 - 152)	5	(0 - 10)
Red Dell Beck	115	(104 - 127)	84	(76 - 92)	116	(105 - 128)	9	(4 - 14)
Torver Beck	163	(147 - 180)	57	(51 - 63)	97	(87 - 107)	4	(0 - 9)
Washfall Beck	176	(159 - 194)	56	(51 - 62)	113	(102 - 125)	4	(0 - 9)
Stony Beck	114	(103 - 125)	56	(50 - 61)	107	(96 - 118)	2	(0 - 7)
Hagg Gill	197	(177 - 217)	47	(42 - 52)	90	(81 - 100)	3	(0 - 8)
Trout Beck	126	(114 - 139)	32	(27 - 37)	81	(73 - 89)	2	(0 - 7)
Woundale Beck	107	(96 - 117)	43	(38 - 48)	99	(89 - 108)	2	(0 - 7)
Hall Gill	212	(190 - 233)	110	(99 - 121)	191	(172 - 210)	2	(0 - 7)
River Mint Trib	218	(196 - 240)	84	(75 - 92)	114	(103 - 126)	5	(0 - 10)
Borrow Beck	184	(165 - 202)	63	(57 - 70)	129	(116 - 142)	5	(0 - 10)
Bannisdale Beck	177	(159 - 194)	87	(78 - 96)	146	(131 - 160)	4	(0 - 9)
River Sprint	210	(189 - 231)	41	(36 - 46)	70	(63 - 77)	3	(0 - 8)
Moasdale Beck	34	(29 - 39)	31	(26 - 36)	108	(97 - 119)	4	(0 - 9)
Castle How Beck	104	(94 - 115)	63	(57 - 69)	181	(163 - 199)	4	(0 - 9)
Tarn Beck	81	(73 - 89)	49	(44 - 54)	113	(102 - 124)	4	(0 - 9)
Sling Beck	56	(50 - 62)	40	(35 - 45)	98	(88 - 108)	1	(0 - 6)
Holehouse Gill	123	(111 - 135)	69	(62 - 76)	114	(103 - 126)	4	(0 - 9)
Crosby Gill	126	(114 - 139)	53	(47 - 58)	115	(103 - 126)	4	(0 - 9)
Greendale Gill	83	(75 - 91)	87	(78 - 96)	196	(176 - 216)	5	(0 - 10)
Nether Beck	91	(82 - 100)	62	(56 - 69)	176	(158 - 194)	5	(0 - 10)
Whillan Beck	89	(80 - 97)	65	(59 - 72)	167	(151 - 184)	5	(0 - 10)
Hardknott Gill	159	(143 - 175)	46	(41 - 51)	122	(110 - 134)	4	(0 - 9)
Whelpside Ghyll	156	(140 - 171)	49	(44 - 54)	164	(147 - 180)	1	(0 - 6)
Wyth Burn	107	(96 - 117)	28	(23 - 33)	82	(73 - 90)	1	(0 - 6)
Launchy Ghyll	104	(93 - 114)	22	(17 - 27)	82	(73 - 90)	1	(0 - 60
Shoulthwaite Gill	202	(181 - 222)	42	(37 - 47)	119	(107 - 131)	2	(0 - 7)
Coledale Beck	199	(179 - 219)	76	(68 - 83)	157	(142 - 173)	5	(0 - 10)
Liza Beck	23	(18 - 28)	51	(46 - 56)	129	(116 - 142)	4	(0 - 9)
Mill Beck 2	110	(99 - 121)	51	(46 - 56)	112	(101 - 123)	2	(0 - 7)
Sour Milk Gill	66	(60 - 73)	32	(27 - 37)	109	(98 - 120)	1	(0 - 6)
Styhead Gill	120	(108 - 132)	29	(24 - 34)	72	(64 - 79)	3	(0 - 8)
Glenridding Beck	138	(124 - 152)	44	(39 - 49)	97	(87 - 106)	1	(0 - 6)
Glencoyne Beck	184	(166 - 202)	44	(39 - 49)	91	(82 - 100)	2	(0 - 7)
Aira Beck	134	(120 - 147)	42	(37 - 47)	103	(93 - 113)	1	(0 - 6)
Parkhouse Gill	281	(253 - 309)	94	(85 - 103)	109	(98 - 120)	6	(1 - 11)
Fusedale Beck	200	(180 - 220)	49	(44 - 54)	71	(64 - 78)	3	(0 - 8)
Heltondale Beck	199	(179 - 219)	81	(73 - 89)	88	(79 - 97)	5	(0 - 10)
Cawdale Beck	154	(139 - 170)	57	(52 - 63)	84	(75 - 92)	4	(0 - 9)
Gatescarth Beck	188	(170 - 207)	55	(50 - 61)	65	(58 - 71)	1	(0 - 6)
Naddle Beck	251	(226 - 276)	57	(51 - 63)	88	(79 - 97)	1	(0 - 6)
Mosedale Beck	164	(148 - 180)	64	(58 - 70)	69	(62 - 76)	1	(0 - 6)
Tailbert Gill	292	(262 - 321)	133	(119 - 146)	155	(139 - 170)	7	(2 - 12)

Table G7 - The weighted soil exchangeable base cation concentrations and the target 'windows' for each site. (Units are %)

Sample	Ca	Ca window	Mg	Mg window	Na	Na window	K	K window
Rydal Beck	7.3	(6.8 - 7.8)	5.9	(5.4 - 6.4)	0.3	(0.0 - 0.8)	0.8	(0.3 - 1.3)
Stock Ghyll	3.5	(3.0 - 4.0)	2.5	(2.0 - 3.0)	0.6	(0.1 - 1.1)	0.7	(0.2 - 1.2)
Dale Park Beck	8.3	(7.8 - 8.8)	6.2	(5.7 - 6.7)	0.4	(0.0 - 0.9)	0.7	(0.2 - 1.2)
Low Cunsey Beck	7.5	(7.0 - 8.0)	1.9	(1.4 - 2.4)	0.8	(0.3 - 1.3)	0.8	(0.3 - 1.3)
Belle Grange Beck	3.6	(3.1 - 4.1)	2.6	(2.1 - 3.1)	0.6	(0.1 - 1.1)	0.7	(0.2 - 1.2)
Red Dell Beck	0.5	(0.0 - 1.0)	0.9	(0.4 - 1.4)	0.9	(0.4 - 1.4)	0.5	(0.0 - 1.0)
Torver Beck	1.8	(1.3 - 2.3)	1.3	(0.8 - 1.8)	0.7	(0.2 - 1.2)	0.7	(0.2 - 1.2)
Washfall Beck	6.7	(6.2 - 7.2)	5.0	(4.5 - 5.5)	0.5	(0.0 - 1.0)	0.7	(0.2 - 1.2)
Stony Beck	9.8	(9.3 - 10.3)	7.4	(6.9 - 7.9)	0.4	(0.0 - 0.9)	0.7	(0.2 - 1.2)
Hagg Gill	14.8	(14.3 - 15.3)	10.9	(10.4 - 11.4)	0.1	(0.0 - 0.6)	0.7	(0.2 - 1.2)
Trout Beck	7.2	(6.7 - 7.7)	5.6	(5.1 - 6.1)	0.2	(0.0 - 0.7)	0.7	(0.2 - 1.2)
Woundale Beck	4.5	(4.0 - 5.0)	3.6	(3.1 - 4.1)	0.5	(0.0 - 1.0)	0.8	(0.3 - 1.3)
Hall Gill	7.7	(7.2 - 8.2)	4.9	(4.4 - 5.4)	0.4	(0.0 - 0.9)	0.5	(0.0 - 1.0)
River Mint Trib	0.5	(0.0 - 1.0)	0.9	(0.4 - 1.4)	0.9	(0.4 - 1.4)	0.5	(0.0 - 1.0)
Borrow Beck	16.1	(15.6 - 16.6)	10.2	(9.7 - 10.7)	0.0	(0.0 - 0.5)	0.3	(0.0 - 0.8)
Bannisdale Beck	10.9	(10.4 - 11.4)	6.0	(5.5 - 6.5)	0.1	(0.0 - 0.6)	0.1	(0.0 - 0.6)
River Sprint	9.7	(9.2 - 10.2)	6.3	(5.8 - 6.8)	0.2	(0.0 - 0.7)	0.5	(0.0 - 1.0)
Moasdale Beck	6.5	(6.0 - 7.0)	3.8	(3.3 - 4.3)	0.3	(0.0 - 0.8)	0.5	(0.0 - 1.0)
Castle How Beck	9.0	(8.5 - 9.5)	7.1	(6.6 - 7.6)	0.3	(0.0 - 0.8)	0.8	(0.3 - 1.3)
Tarn Beck	1.6	(1.1 - 2.1)	1.6	(1.1 - 2.1)	0.5	(0.0 - 1.0)	0.9	(0.4 - 1.4)
Sling Beck	7.4	(6.9 - 7.9)	5.4	(4.9 - 5.9)	0.4	(0.0 - 0.9)	0.7	(0.2 - 1.2)
Holehouse Gill	9.4	(8.9 - 9.9)	5.3	(4.8 - 5.8)	0.2	(0.0 - 0.7)	0.4	(0.0 - 0.9)
Crosby Gill	5.5	(5.0 - 6.0)	3.3	(2.8 - 3.8)	0.4	(0.0 - 0.9)	0.6	(0.1 - 1.1)
Greendale Gill	11.2	(10.7 - 11.7)	5.4	(4.9 - 5.9)	0.6	(0.1 - 1.1)	0.8	(0.3 - 1.3)
Nether Beck	3.9	(3.4 - 4.4)	3.4	(2.9 - 3.9)	0.4	(0.0 - 0.9)	0.9	(0.4 - 1.4)
Whillan Beck	9.7	(9.2 - 10.2)	6.3	(5.8 - 6.8)	0.2	(0.0 - 0.7)	0.5	(0.0 - 1.0)
Hardknott Gill	5.6	(5.1 - 6.1)	4.6	(4.1 - 5.1)	0.4	(0.0 - 0.9)	0.8	(0.3 - 1.3)
Whelpside Ghyll	10.9	(10.4 - 11.4)	7.4	(6.9 - 7.9)	0.2	(0.0 - 0.7)	0.5	(0.0 - 1.0)
Wyth Burn	13.1	(12.6 - 13.6)	8.7	(8.2 - 9.2)	0.1	(0.0 - 0.6)	0.5	(0.0 - 1.0)
Launchy Ghyll	3.5	(3.0 - 4.0)	2.6	(2.1 - 3.1)	0.4	(0.0 - 0.9)	0.8	(0.3 - 1.3)
Shoulthwaite Gill	9.6	(9.1 - 10.1)	7.2	(6.7 - 7.7)	0.2	(0.0 - 0.7)	0.7	(0.2 - 1.2)
Coledale Beck	13.3	(12.8 - 13.8)	10.2	(9.7 - 10.7)	0.1	(0.0 - 0.6)	0.8	(0.3 - 1.3)
Liza Beck	3.9	(3.4 - 4.4)	3.4	(2.9 - 3.9)	0.4	(0.0 - 0.9)	0.9	(0.4 - 1.4)
Mill Beck 2	9.0	(8.5 - 9.5)	7.1	(7.6 - 8.6)	0.3	(0.0 - 0.8)	0.8	(0.3 - 1.3)
Sour Milk Gill	1.4	(0.9 - 1.9)	1.5	(1.0 - 2.0)	0.5	(0.0 - 1.0)	0.9	(0.4 - 1.4)
Styhead Gill	3.9	(3.4 - 4.4)	3.4	(2.9 - 3.9)	0.4	(0.0 - 0.9)	0.9	(0.4 - 1.4)
Glenridding Beck	11.6	(11.1 - 12.1)	6.6	(6.1 - 7.1)	0.1	(0.0 - 0.6)	0.3	(0.0 - 0.8)
Glencoyne Beck	7.8	(7.3 - 8.3)	4.5	(4.0 - 5.0)	0.3	(0.0 - 0.8)	0.4	(0.0 - 0.9)
Aira Beck	6.6	(6.1 - 7.1)	3.8	(3.3 - 4.3)	0.3	(0.0 - 0.8)	0.2	(0.0 - 0.7)
Parkhouse Gill	1.5	(1.0 - 2.0)	1.2	(0.7 - 1.7)	0.6	(0.1 - 1.1)	0.8	(0.3 - 1.3)
Fusedale Beck	15.1	(14.6 - 15.6)	10.5	(10.0 - 11.0)	0.1	(0.0 - 0.6)	0.5	(0.0 - 1.0)
Heltondale Beck	5.1	(4.6 - 5.6)	4.1	(3.6 - 4.6)	0.3	(0.0 - 0.8)	0.4	(0.0 - 0.9)
Cawdale Beck	13.2	(12.7 - 13.7)	8.8	(8.3 - 9.3)	0.1	(0.0 - 0.6)	0.3	(0.0 - 0.8)
Gatescarth Beck	6.3	(5.8 - 6.8)	3.8	(3.3 - 4.3)	0.3	(0.0 - 0.8)	0.6	(0.1 - 1.1)
Naddle Beck	6.5	(6.0 - 7.0)	4.0	(3.5 - 4.5)	0.3	(0.0 - 0.8)	0.6	(0.1 - 1.1)
Mosedale Beck	11.0	(10.5 - 11.5)	6.5	(6.0 - 7.0)	0.2	(0.0 - 0.7)	0.4	(0.0 - 0.9)
Tailbert Gill	0.5	(0.0 - 1.0)	0.9	(0.4 - 1.4)	0.9	(0.4 - 1.4)	0.5	(0.0 - 1.0)

G.2.3 The output from each site after optimisation procedure

Ten calibrations were carried out at each site using the optimisation algorithm. Using data from only the successful calibrations, the average catchment weathering rate and initial soil (i.e. 1856) base saturation can be calculated for each site, these can be found in Table G8 and G9 respectively. The data for the individual calibrations are available from the author on request.

Table G8 - Mean catchment weathering rates derived from the successful MAGIC calibrations for each site (Units are $\mu eq\ m^{-2}\ yr^{-1}$)

Sample	We Ca	We Mg	We Na	We K	Total Weathering
Rydal Beck	240.65	45.14	0.82	0	286.61
Stock Ghyll	340.99	1.19	0	0	342.18
Dale Park Beck	227.68	0.32	5.32	0.11	233.43
Low Cunsey Beck	355.16	19.98	0	0.02	375.16
Belle Grange Beck	225.54	0.59	8.74	0.14	235.01
Red Dell Beck	201.3	133.54	70.33	11.66	416.83
Torver Beck	224.69	14.69	7.33	0.01	246.72
Washfall Beck	217.67	22.64	55.36	0.57	296.24
Stony Beck	79.22	15.48	60.32	0.08	155.1
Hagg Gill	248.01	2.65	1.95	0.46	253.07
Trout Beck	167.86	0.35	29.32	0.08	197.61
Woundale Beck	110.55	5.07	29.8	0	145.42
Hall Gill	274.59	122.36	198.79	0.25	595.99
River Mint Trib	248.78	69.89	0.05	3.03	321.75
Borrow Beck	212.67	17.2	4.75	1.24	235.86
Bannisdale Beck	228.75	91.66	134.27	0.99	455.67
River Sprint	321.49	2.28	0.05	0.56	324.38
Moasdale Beck	0.57	4.33	69.03	1.92	75.85
Castle How Beck	107.56	4.48	31.3	0.2	143.54
Tarn Beck	112.22	46.65	33.25	0.23	192.35
Sling Beck	27.04	10.27	28	0	65.31
Holehouse Gill	108.09	36.93	17.62	0.42	163.06
Crosby Gill	117.82	11.85	35.19	0.2	165.06
Greendale Gill	50.13	49.23	16.8	0.22	116.38
Nether Beck	143.09	41.71	25.43	1.34	211.57
Whillan Beck	76.92	18.7	19.53	0.66	115.81
Hardknott Gill	261.95	0	0.11	0.24	262.3
Whelpside Ghyll	229.06	3.37	36.45	0	268.88
Wyth Burn	159.79	0	24.76	0.01	184.56
Launchy Ghyll	192.61	0	1.7	0	194.31
Shoulthwaite Gill	303.13	0.11	1.07	0.08	304.39
Coledale Beck	292.71	15.03	0.05	0.08	307.87
Liza Beck	0	47.95	35.2	0.99	84.14
Mill Beck 2	154.43	9.43	0.1	0.01	163.97
Sour Milk Gill	144.99	18.42	53.54	0.41	217.36
Styhead Gill	361.88	8.19	1.36	3.1	374.53
Glenridding Beck	197.14	4.73	7.82	0.13	209.82
Glencoyne Beck	286.32	2.47	0.95	0.01	289.75
Aira Beck	159.14	0.11	5.56	0.01	164.82
Parkhouse Gill	320.32	79.12	53.89	0.88	454.21
Fusedale Beck	217.78	21.12	15.34	0.37	254.61
Heltondale Beck	183.14	51.97	36.46	0.83	272.4
Cawdale Beck	134.05	26.92	28.41	0.97	190.35
Gatescarth Beck	352.55	47.49	11.5	0.39	411.93
Naddle Beck	355.78	27.49	0	0	383.27
Mosedale Beck	210.35	47.02	0.02	0.01	257.4
Tailbert Gill	351.62	145.41	104.15	5.24	606.42

Table G9 - Mean values for initial (1856) exchangeable cation fractions and base saturation derived from the successful MAGIC calibrations for each site
(Units are % of CEC)

Sample	Ca	Mg	Na	K	Base Saturation
Rydal Beck	10.64	8.17	0.49	0.9	20.2
Stock Ghyll	5.7	3.58	0.81	0.76	10.85
Dale Park Beck	14.41	8.41	0.76	0.78	24.36
Low Cunsey Beck	11.96	2.89	1.32	0.8	16.97
Belle Grange Beck	7.02	3.61	0.97	0.84	12.44
Red Dell Beck	15.97	28.54	5.09	2.98	52.58
Torver Beck	5.08	2.94	1.34	0.79	10.15
Washfall Beck	11.39	6.78	0.73	0.81	19.71
Stony Beck	16.43	10.71	0.74	0.83	28.71
Hagg Gill	24.54	13.52	0.44	0.82	39.32
Trout Beck	19.27	9.63	0.52	0.92	30.34
Woundale Beck	8.72	5.44	0.77	0.9	15.83
Hall Gill	10.41	6.4	0.56	0.59	17.96
River Mint Trib	2.33	4.02	2.23	1.34	9.92
Borrow Beck	21.32	12.12	0.33	0.43	34.2
Bannisdale Beck	14.09	7.6	0.38	0.32	22.39
River Sprint	19.24	8.52	0.64	0.68	29.08
Moasdale Beck	9.23	6	0.53	0.68	16.44
Castle How Beck	19.96	14.34	0.66	1.01	35.97
Tarn Beck	9.17	8.42	1.14	1.38	20.11
Sling Beck	10.03	7.28	0.6	0.78	18.69
Holehouse Gill	13.87	7.83	0.5	0.54	22.74
Crosby Gill	9.03	4.84	0.69	0.68	15.24
Greendale Gill	15.54	9.35	0.86	0.95	26.7
Nether Beck	17.33	14.63	0.87	1.58	34.41
Whillan Beck	14.48	9.71	0.5	0.61	25.3
Hardknott Gill	20.98	12.06	0.93	1.26	35.23
Whelpside Ghyll	21.39	12.06	0.59	0.57	34.61
Wyth Burn	20.29	11.07	0.35	0.63	32.34
Launchy Ghyll	11.66	6.76	0.8	1.07	20.29
Shoulthwaite Gill	18.7	10.46	0.57	0.8	30.53
Coledale Beck	22.24	14.4	0.43	1.01	38.08
Liza Beck	8.02	7.68	0.63	1.24	17.57
Mill Beck 2	17.88	11.84	0.55	1.04	31.31
Sour Milk Gill	3.17	3.43	0.77	1.46	8.83
Styhead Gill	20.64	18.06	1.04	1.84	41.58
Glenridding Beck	19.75	9.43	0.44	0.45	30.07
Glencoyne Beck	15.64	6.76	0.61	0.54	23.55
Aira Beck	9.79	4.83	0.54	0.25	15.41
Parkhouse Gill	3.01	2.21	0.88	0.89	6.99
Fusedale Beck	20.4	11.94	0.38	0.59	33.31
Heltondale Beck	7.34	5.15	0.54	0.51	13.54
Cawdale Beck	16.95	10.25	0.38	0.46	28.04
Gatescarth Beck	16.13	7.62	0.78	0.75	25.28
Naddle Beck	12.4	6.17	0.8	0.75	20.12
Mosedale Beck	17.38	9.17	0.63	0.52	27.7
Tailbert Gill	0.97	1.73	1.26	0.8	4.76

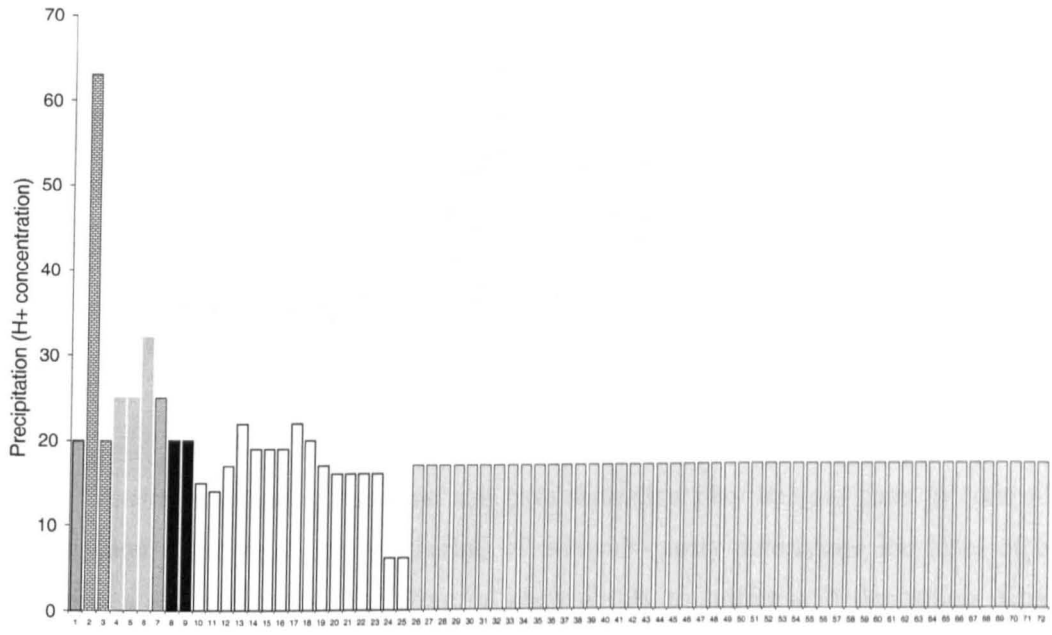
G.3 Comparing Lake District MAGIC application with previous UK work: Study results in context

The MAGIC model has been previously applied to several areas in the UK. It has been applied in Scotland at Dargall Lane (Cosby *et al.*, 1986a), Allt a Mharcaidh (Jenkins *et al.*, 1988), Loch Chon and Kelty Water (Cosby *et al.*, 1990). It has been applied in Wales at Llyn Brianne (Whitehead *et al.*, 1988a, 1990; Waters and Jenkins, 1992) and Plynlimon (Whitehead *et al.*, 1988b; Robson *et al.*, 1991). It has been applied in England at Beacon Hill (Whitehead *et al.*, 1993), Scoat Tarn, Greendale Tarn and Burnmoor Tarn (Barlow, 1994; Whitehead *et al.*, 1997). In addition, site specific applications were carried out for 50 lochs in Galloway, Scotland (Wright *et al.*, 1994) and on the 21 Acid Waters Monitoring Network sites (Jenkins *et al.*, 1997). The MAGIC model has been regionalized using Monte Carlo analysis in Norway (Hornberger *et al.*, 1987). This regional version of MAGIC has also been applied in Wales (Jenkins *et al.*, 1990b) and Scotland (Musgrove *et al.*, 1990).

Figure G7 - A location map of the sites to which MAGIC was applied during the eight previous studies.

The present study examines a wide range of streams with variable degrees of sensitivity to acidification. To put the present work in context, the hydrogen deposition, stream alkalinity, soil base saturation and base cation weathering rates were examined from the present study and the eight previous studies to which MAGIC had been applied (see location map – Figure G7). The streams and lakes from the previous work had been chosen specifically by their investigators because they were sensitive to acidification, therefore, the alkalinity of these sites was very low (< 50 μeq l^{-1}).

Figure G8 - H^+ deposition for eight previous UK studies and the current study.
(Site 1 – Robson et al, 1991; Sites 2-3 – Whitehead et al, 1988a; Sites 4-6 – Cosby et al, 1986a & 1990; Site 7 – Jenkins et al, 1988; Sites 8-9 – Barlow, 1994; Sites 10-25 – Jenkins et al, 1997; Sites 26-72 – This study).

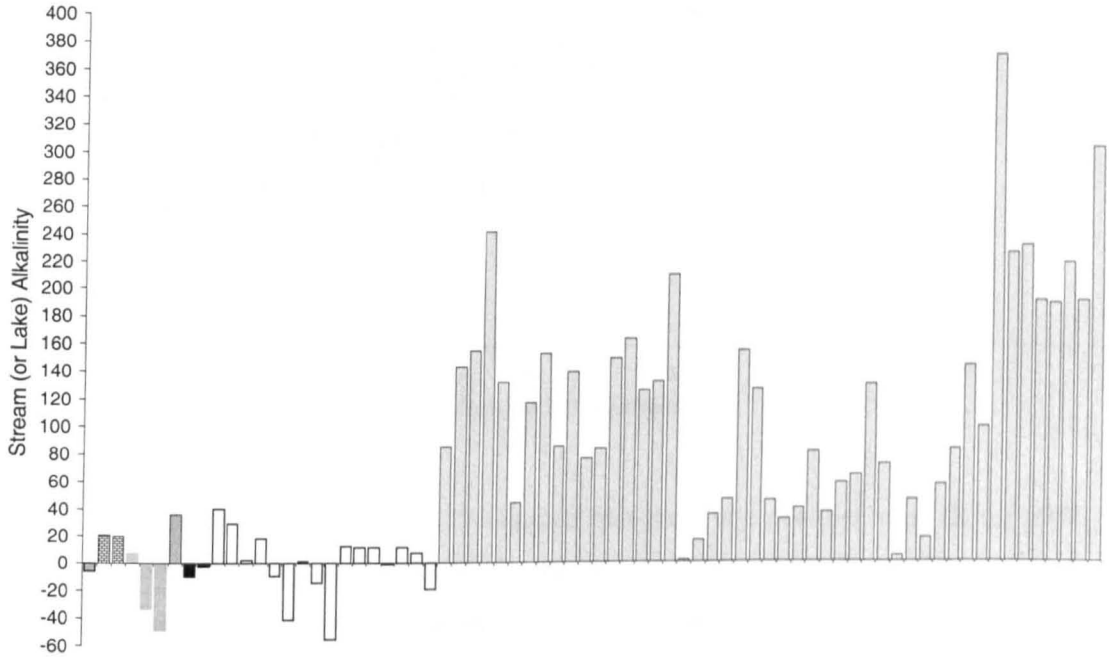


The pH of deposition at the sites was transformed into hydrogen concentrations (Figure G8). The precipitation data for the current study is the same for every site because the sea-salt and dry deposition corrections (which maintain the pH of precipitation) are based on one monitoring site. In general, hydrogen concentrations range between 15 and 25 μeq l^{-1}, but Afon Cyff in Wales (Whitehead *et al.*, 1988a) and Kelty Water in Scotland (Cosby *et al.*, 1990) have higher hydrogen concentrations (63 and 32 μeq l^{-1} respectively). There are also two low deposition sites, Bencrom River and Blue Lough (Jenkins *et al.*, 1997) which receive a hydrogen concentration of 6 μeq l^{-1}.

In contrast to hydrogen deposition, the stream water alkalinity is quite variable across the comparison sites (Figure G9), with alkalinity ranging between –56 and 46 μeq l^{-1}.

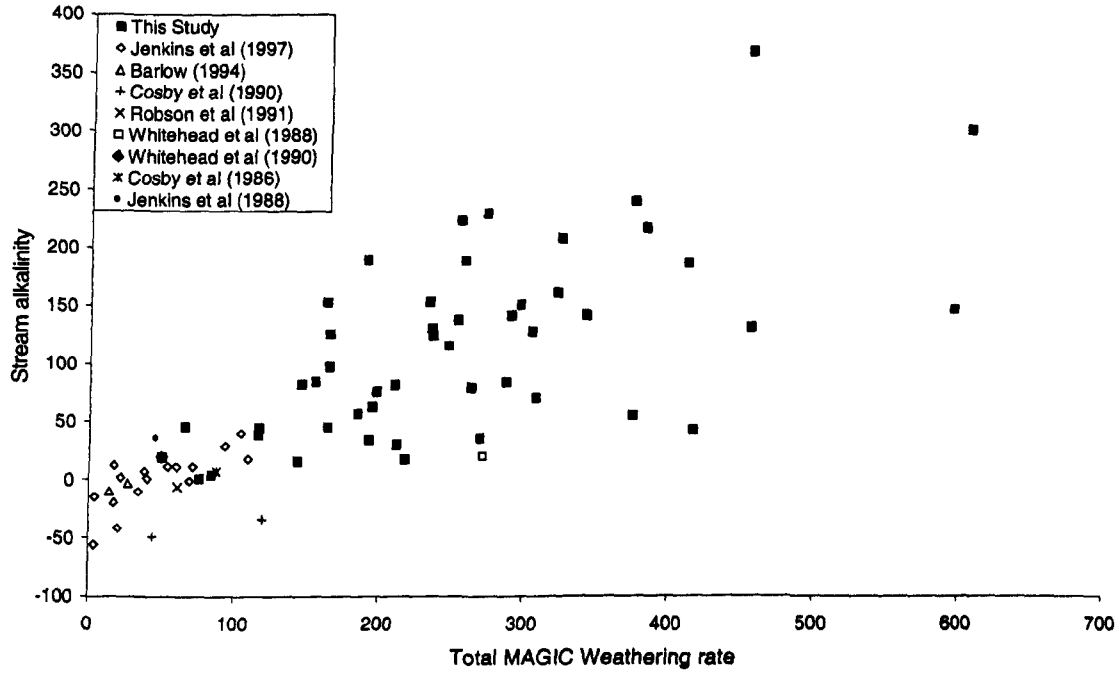
Afon Cyff (the site with the most hydrogen deposition) has an alkalinity of 20 μeq l^{-1}, whereas Blue Lough and Bencrom River (the low hydrogen deposition sites) have alkalinities of –20 and 7 μeq l^{-1}.

Figure G9 - Stream alkalinity against Hydrogen precipitation for the Lake District data compared to 8 other UK studies. (Units: μeq l^{-1})



Mineral weathering rates and soil base saturation play integral parts in controlling stream water chemistry. The weathering of minerals partly determines the level of base saturation a soil possesses. Therefore, a site's ability to buffer acid deposition depends ultimately on the amount of mineral weathering that occurs. If the weathering rate outstrips the rate of input of acids, then equilibrium will prevail. However, if the input of acids outstrips the rate of weathering, then progressive acidification will occur.

Figure G10 - Stream alkalinity against MAGIC weathering rates for the eight previous UK studies and the current study. (Units: alkalinity – μeq l^{-1}, weathering rates – μeq m^{-2} yr^{-1})

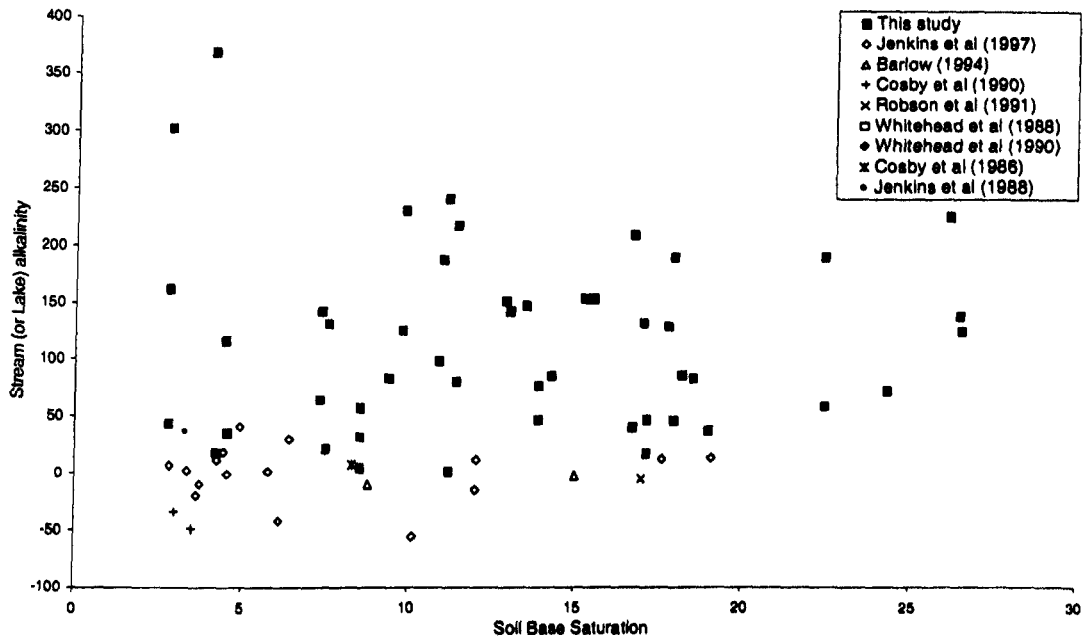


The examination of Figure G10 suggests that there is a positive trend (R^2 of 60%) between stream alkalinity and modelled weathering rates (i.e. as weathering rates increase so does the alkalinity). However, the majority of the Lake District sites fall outside the range of data from the previous work, with higher weathering rates than the comparative sites. This is because the streams and lakes from the previous work were chosen specifically because of their sensitivity to acidification (i.e. low alkalinities). In general, the comparison sites have low total MAGIC weathering rates, ranging between 4 and 120 μeq m^{-2} yr^{-1}. This suggests that these sites are extremely susceptible to acidification. However, Afon Cyff (Whitehead *et al.*, 1988a) has a MAGIC weathering rate of 271 μeq m^{-2} yr^{-1} but still has a very low alkalinity (21 μeq l^{-1}). In addition, thirty-six of the Lake District sites have higher weathering rates than the bulk of the comparison sites (> 120 μeq m^{-2} yr^{-1}) and still have low alkalinity's (< 200 μeq l^{-1}). This might suggest that despite the high weathering rates progressive freshwater acidification is taking place.

Previous work suggests that acid rain has a profound effect on weathering rates (Paces, 1986; Wright, 1988; Bricker *et al.*, 1994; Johnson *et al.*, 1994), which suggest elevated acid inputs increase the rate of chemical weathering in catchments underlain by reactive rock types and cause progressive acidification of water and soil in catchments underlain by non-reactive rock types. However, the weathering of minerals can occur at a very high rate to provide dissolved cations to the soil complex and yet acid deposition inputs can still

reduce the buffering capacity. For example, Red Dell Beck has one of the highest modelled weathering rates (417 $\mu eq\ m^{-2}\ yr^{-1}$), but it has a low stream alkalinity (43 $\mu eq\ l^{-1}$) and a low base saturation (3%). Despite the high modelled weathering rate, the simulated base saturation at Red Dell Beck has declined from 53% in 1856 to an actual base saturation of 3% in 1996. This indicates that at this particular site, the acid inputs from precipitation outweigh the provision of base cations by weathering (i.e. the occurrence of progressive acidification).

Figure G11 - Stream alkalinity against Soil base saturation for the eight previous UK studies and the current study. (Units: Alkalinity is $\mu eq\ l^{-1}$, Base saturation is %)



Looking at MAGIC weathering rates has helped to examine one of the underlying processes governing buffering. An examination of the soil base saturation of the sites gives us another method of assessing the stream's susceptibility to acidification. There is significant variability in the soil base saturation values, forty-one of the Lake District sites fall within the range of data from the previous work and six sites have a higher base saturation than the comparative sites (Figure G11). The majority of the comparison exercise sites have a soil base saturation ranging between 0 and 10%, suggesting susceptibility to acidification. Afon Gwy (Robson *et al.*, 1991), Narrator Brook, Llyn Llagi (Jenkins *et al.*, 1997), Greendale Tarn (Barlow, 1994) and eighteen of the Lake District sites have a base saturation above 15% indicating that buffering against acid deposition should be available. However, the stream alkalinity of the high base saturation sites (> 15%) is generally quite

low (< 200 μeq l^{-1}) which could suggest that progressive acidification of the freshwater ecosystem is occurring. On the whole, the large range of values suggests that, in terms of stream alkalinity, soil base saturation doesn't play such an important role as weathering rates.

All of the sites examined during the comparison exercise are suffering from progressive acidification, but they are acidifying at distinct rates. The weathering rates, base saturation and streamwater chemistry are variable, which reflects the heterogeneous nature of stream and lake catchments. When considering each catchment it must be remembered that the initial conditions weren't the same. Some may have reactive rock types, whilst others may have non-reactive rock types. In addition, each catchment has experienced diverse acid deposition loads over different timescales. Bearing this in mind, it is important to identify sites that are degrading the fastest, as well as the sites that were initially sensitive and have only altered a small amount.

APPENDIX H

Statistical Results

H.1 Generation and testing of 'secondary' regression models

H.1.1 Testing 'Geology only', 'Soil only', 'Land Use only' and 'Deposition only' models

In the first step, the full dataset of water chemistry concentrations (i.e. 55 catchments over the six surveys – n = 330) were related to the percentage areal coverage of only the five geology groups (Table H1). The R-squared (R^2) values ranged between 0.079 (silica) and 0.270 (nitrate) with upto three, but occasionally as few as one, predictor variables for the 'geology only' model. The highest R^2 was found between nitrate and two predictor variables (0.270), which means that 27% of the variation in nitrate concentrations can be explained by the two catchment parameters selected by the stepwise method.

Table H1 – Stepwise regression analyses of the 6 survey 'Geology only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.997		-
	SKS	-0.006	12.20	6.89
	SIL	0.002		3.68
	GR	-0.007		1.63
Sodium	Intercept	152.50		-
	BVG	-0.46	14.86	11.95
	GR	1.01		2.91
Magnesium	Intercept	93.96		-
	BVG	-0.33	10.37	8.30
	MIX	1.04		2.07
Calcium	Intercept	162.00		-
	SIL	1.86	26.00	26.00
Potassium	Intercept	4.36		-
	SIL	0.07	12.87	12.87
Chloride	Intercept	181.30		-
	BVG	-0.68	21.12	14.67
	MIX	-1.64		3.90
	GR	1.13		2.55
Nitrate	Intercept	9.28		-
	SIL	0.44	26.95	24.89
	MIX	-0.62		2.06
Sulphate	Intercept	111.9		-
	BVG	-0.39	14.27	14.27
Alkalinity	Intercept	116.50		-
	SIL	1.31	13.16	11.01
	MIX	3.10		3.15
Silica	Intercept	158.90		-
	SIL	0.51	7.99	7.99

This process was repeated using the percentage areal coverage of only the four soil

types (Table H2), then only the three land uses (Table H3), and finally, only the seven 20 x 20km grid deposition loads (Table H4).

Table H2 – Stepwise regression analyses of the 6 survey 'Soil only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	7.732		-
	PTY	-0.092	4.65	3.21
	THP	-0.008		1.44
Sodium	Intercept	115.9		-
	THP	1.19	11.79	10.59
	THI	0.71		1.20
Magnesium	Intercept	56.19		-
	THP	0.91	11.79	8.79
	GLY	1.19		3.00
Calcium	Intercept	136.30		-
	THP	3.88	23.75	22.55
	GLY	1.95		1.20
Potassium	Intercept	3.11		-
	THP	0.17	16.20	16.20
Chloride	Intercept	125.10		-
	THP	1.64	15.77	13.83
	THI	-1.07		1.94
Nitrate	Intercept	-0.74		-
	SIL	1.16	35.28	35.28
Sulphate	Intercept	81.18		-
	THP	0.98	12.99	10.60
	THI	-0.78		2.39
Alkalinity	Intercept	301.40		-
	PTY	-2.23	10.19	10.19
Silica	Intercept	210.70		
	PTY	-0.60	4.02	4.02

Table H3 – Stepwise regression analyses of the 6 survey 'Land Use only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.909		-
	AGR	0.006	8.34	8.34
Sodium	Intercept	167.50		-
	UPL	-0.53	9.83	9.83
Magnesium	Intercept	64.26		-
	AGR	0.72	12.97	12.97
Calcium	Intercept	155.80		-
	AGR	3.04	35.75	33.74
	FOR	1.00		2.01
Potassium	Intercept	4.25		-
	AGR	0.12	19.33	19.33
Chloride	Intercept	191.30		-
	UPL	-0.69	11.63	11.63
Nitrate	Intercept	6.23		-
	AGR	0.78	41.28	40.46
	FOR	0.15		0.82
Sulphate	Intercept	140.20		-
	UPL	-0.62	9.89	8.04
	AGR	-0.36		1.85
Alkalinity	Intercept	112.50		-
	AGR	2.85	22.95	22.95
Silica	Intercept	239.50		-
	UPL	-0.87	17.08	17.08

Table H4 – Stepwise regression analyses of the 6 survey 'Deposition only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.764		-
	DEP3	0.006		7.46
	DEP6	0.004	**13.74**	4.92
	DEP5	0.002		1.36
Sodium	Intercept	124.00		-
	DEP3	0.51		9.49
	DEP6	-0.21	**15.10**	3.54
	DEP4	0.39		2.07
Magnesium	Intercept	81.95		-
	DEP3	0.45		11.20
	DEP7	-0.38	**17.38**	4.50
	DEP5	-0.22		1.68
Calcium	Intercept	163.70		-
	DEP3	2.63		29.55
	DEP6	0.49	**33.24**	2.70
	DEP4	-0.67		0.99
Potassium	Intercept	5.46		-
	DEP3	0.09	**18.55**	16.99
	DEP7	-0.02		1.56
Chloride	Intercept	140.90		-
	DEP6	-0.42		12.98
	DEP3	0.57	**20.34**	5.49
	DEP4	0.44		1.87
Nitrate	Intercept	8.83		-
	DEP3	0.69	**41.01**	40.26
	DEP5	0.08		0.75
Sulphate	Intercept	80.59		-
	DEP3	0.27	**4.16**	2.93
	DEP5	0.14		1.23
Alkalinity	Intercept	78.29		-
	DEP3	2.69		17.28
	DEP6	1.23	**28.55**	8.73
	DEP1	1.49		2.54
Silica	Intercept	173.90		-
	DEP7	-0.44		10.65
	DEP3	0.46	**16.46**	3.23
	DEP2	0.53		2.58

The R-squared (R^2) values ranged between 0.040 (silica) and 0.353 (nitrate) with upto two predictor variables for the 'soil only' model, 0.083 (pH) and 0.413 (nitrate) with upto two predictor variables for the 'land use only' model, and 0.042 (sulphate) and 0.410 (nitrate) with upto three predictor variables for the 'deposition only' model. The highest R^2 values were always found between nitrate and 1-2 predictor variables (0.353 with 1 predictor in the 'soil only' model, 0.413 with 2 predictors in the 'land use only' model, and 0.410 with 2 predictors in the 'deposition only' model respectively).

In the second step, the full dataset of water chemistry 'fluxes' (i.e. mean annual flow-weighted concentrations of the study catchments – n = 55) were related to the percentage areal coverage of only the five geology groups (Table H5). The R-squared (R^2) values ranged between 0.145 (silica) and 0.393 (calcium) with upto two predictor variables for the 'geology only' model. The highest R^2 was found between calcium and one predictor variable (0.393), which means that 39% of the variation in flow-weighted calcium concentrations can be explained by the one catchment parameter selected by the stepwise

method.

Table H5 – Stepwise regression analyses of the flow-weighted 'Geology only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.292		-
	SIL	0.008	**28.80**	19.80
	BVG	0.005		9.00
Sodium	Intercept	135.90		-
	BVG	-0.31	**23.51**	13.52
	GR	1.18		9.99
Magnesium	Intercept	76.51		-
	BVG	-0.24	**19.25**	19.25
Calcium	Intercept	144.0		-
	SIL	1.53	**39.32**	39.32
Potassium	Intercept	3.03		-
	SIL	0.06	**32.47**	32.47
Chloride	Intercept	153.90		-
	BVG	-0.46	**22.96**	15.39
	GR	1.45		7.57
Nitrate	Intercept	8.41		-
	SIL	0.40	**23.60**	23.60
Sulphate	Intercept	97.93		-
	BVG	-0.31	**18.38**	18.38
Alkalinity	Intercept	109.20		-
	SIL	1.30	**28.34**	28.34
Silica	Intercept	154.60		-
	SIL	0.56	**14.53**	14.53

This process was repeated using the percentage areal coverage of only the four soil types (Table H6), then only the three land uses (Table H7), and finally, only the seven Cl-balance deposition loads (Table H8).

Table H6 – Stepwise regression analyses of the flow-weighted 'Soil only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	7.100		-
	PTY	-0.005	**10.60**	10.60
Sodium	Intercept	108.50		-
	THP	0.65	**9.93**	9.93
Magnesium	Intercept	52.01		-
	THP	0.56	**17.68**	17.68
Calcium	Intercept	123.30		-
	THP	3.46	**38.50**	38.50
Potassium	Intercept	1.86		-
	THP	0.15	**43.59**	43.59
Chloride	Intercept	108.80		-
	THP	1.15	**15.47**	15.47
Nitrate	Intercept	-0.87		-
	THP	1.12	**36.53**	36.53
Sulphate	Intercept	67.23		-
	THP	0.64	**13.00**	13.00
Alkalinity	Intercept	279.10		-
	SIL	-2.10	**26.49**	26.49
Silica	No variables	N/A	N/A	N/A

Table H7 – Stepwise regression analyses of the flow-weighted 'Land Use only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.680		-
	AGR	0.007	**26.02**	26.02
Sodium	No variables	N/A	**N/A**	N/A
Magnesium	Intercept	55.34		-
	AGR	0.40	**23.85**	23.85
Calcium	Intercept	237.90		-
	AGR	1.48	**54.56**	50.09
	UPL	-1.00		4.47
Potassium	Intercept	2.92		-
	AGR	0.10	**49.65**	49.65
Chloride	Intercept	165.70		-
	UPL	-0.48	**10.10**	10.10
Nitrate	Intercept	7.10		-
	AGR	0.73	**39.89**	39.89
Sulphate	Intercept	74.62		-
	FOR	0.58	**14.52**	14.52
Alkalinity	Intercept	103.20		-
	AGR	2.51	**52.50**	52.50
Silica	Intercept	238.60		-
	UPL	-0.89	**27.04**	27.04

Table H8 – Stepwise regression analyses of the flow-weighted 'Deposition only' model

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.626		-
	DEP3	0.005	**25.79**	14.72
	DEP6	0.003		11.07
Sodium	Intercept	126.70		-
	DEP6	-0.23	**8.07**	8.07
Magnesium	Intercept	63.99		-
	DEP7	-0.22	**31.11**	21.38
	DEP3	0.23		9.73
Calcium	Intercept	157.90		-
	AGR	1.88	**38.63**	38.63
Potassium	Intercept	3.40		-
	DEP3	0.08	**43.48**	43.48
Chloride	Intercept	143.70		-
	DEP6	-0.50	**18.64**	18.64
Nitrate	Intercept	10.36		-
	DEP3	0.62	**37.01**	37.01
Sulphate	No variables	N/A	**N/A**	N/A
Alkalinity	Intercept	95.86		-
	DEP3	2.01	**42.14**	33.92
	DEP6	0.65		8.22
Silica	Intercept	172.70		-
	DEP7	-0.42	**20.26**	13.04
	DEP3	0.50		7.22

The R-squared (R^2) values ranged between < 0.04 (silica) and 0.436 (potassium) with one predictor variable for the 'soil only' model, < 0.04 (sodium) and 0.546 (calcium) with upto two predictor variables for the 'land use only' model, and < 0.04 (sulphate) and 0.434 (potassium) with upto two predictor variables for the 'deposition only' model. The highest R^2 value was found in the 'land use only' model between calcium and 2 predictor

variables (0.546). In addition, potassium recorded the highest R^2 values in the 'soil only' model (0.436 with 1 predictor) and in the 'deposition only' model (0.434 with 1 predictor).

Summary

In the '6 survey' dataset, both land use and deposition variables account for around 41% of the variation in water chemistry concentrations and soil variables account for roughly 35%, whereas geological variables only account for 27% of the variation. In the 'flow-weighted' dataset, land use variables account for around 55% of the variation in annual water chemistry concentrations, soil and deposition variables account for roughly 44%, whereas geological variables only account for 39% of the variation. From this it can be suggested that land use variables are the most important, and geological variables are the least important, factors controlling the streamwater chemistry of the Lake District. All the catchment characteristics were used in a stepwise regression model to test this hypothesis.

H.1.2 Testing full models (i.e. all catchment characteristics and sites)

Stepwise multiple regression was carried out on the '6 survey' and 'flow-weighted' datasets to ascertain which are the important variables controlling Lake District streamwater chemistry. The variables used in the regression analyses are tabulated in Table H9.

Table H9 – Catchment variables used in the stepwise regression models

Catchment variables	'6 Survey' multiple regression *(All sites)*	'6 Survey' multiple regression *(w/o agr sites)*	'Flow-weighted' multiple regression *(All sites)*	'Flow-weighted' multiple regression *(w/o agr sites)*
BVG	√	√	√	√
SIL	√	√	√	√
SKS	√	√	√	√
GR	√	√	√	√
MIX	√	√	√	√
UPL	√	√	√	√
FOR	√	√	√	√
AGR	√	√	√	√
THP	√	√	√	√
THI	√	√	√	√
GLY	√	√	√	√
PTY	√	√	√	√
DEP1	√	√		
DEP2	√	√		
DEP3	√			
DEP4	√	√		
DEP5	√	√		
DEP6	√	√		
DEP7	√	√		
CLDEP1			√	
CLDEP2			√	√
CLDEP3			√	√
CLDEP4			√	√
CLDEP5			√	√
CLDEP6			√	√
CLDEP7			√	√
S&N dep				
Discharge	√	√		
Ann Rainfall			√	√
Ann Runoff			√	√
Site altitude	√	√	√	√
Max altitude	√	√	√	√
Dist to sea	√	√	√	√

The full '6 survey' dataset of water chemistry concentrations (n = 330) were related to the 23 predictor variables (Table H10).

Table H10 – Stepwise regression analyses of the full '6 survey' dataset (n=330)

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.561		.
	Sea	0.027		17.66
	Max Alt	-0.001	33.98	8.25
	SKS	-0.007		2.73
	DEP2	0.004		2.54
	DEP7	-0.003		1.36
	DEP6	-0.002		1.34
Sodium	Intercept	138.20		.
	Sea	-1.03		11.95
	DEP3	0.41	23.86	3.80
	GR	1.11		2.85
	FOR	0.69		1.84
	THP	0.61		1.79
	DEP5	-0.20		1.65
Magnesium	Intercept	70.10		.
	AGR	0.59		12.97
	MIX	1.35	22.98	5.49
	DEP7	-0.24		2.02
	DEP5	-0.17		1.47
	GLY	0.72		1.03
Calcium	Intercept	203.07		.
	Sea	4.00		33.74
	Max Alt	-0.12	46.07	5.76
	DEP3	1.43		3.97
	UPL	-0.82		2.60
Potassium	Intercept	3.31		.
	AGR	0.09		19.33
	THP	0.07	22.24	1.85
	MIX	0.10		1.06
Chloride	Intercept	139.70		.
	DEP6	-0.43		14.67
	DEP1	-0.49		8.11
	GR	1.61	32.98	4.35
	THP	1.44		2.23
	FOR	0.81		2.11
	DEP5	-0.35		1.23
	THI	-1.07		0.28
Nitrate	Intercept	-63.97		.
	THP	2.47		40.46
	SKS	-0.91		4.53
	MIX	-1.01	56.33	4.45
	PTY	0.76		2.79
	DEP1	0.41		2.36
	DEP5	-0.13		1.74
Sulphate	Intercept	105.20		.
	BVG	-0.33		14.27
	DEP1	-0.54	19.62	2.51
	FOR	0.35		1.64
	SKS	0.28		1.20
Alkalinity	Intercept	169.90		.
	AGR	1.29		22.95
	Sea	4.37		9.49
	Max Alt	-0.26		4.33
	MIX	3.02	42.66	1.54
	SIL	-1.19		1.48
	DEP7	-0.49		1.18
	GLY	2.08		0.98
	DEP3	1.06		0.71
Silica	Intercept	300.40		.
	UPL	-1.63		17.08
	Site Alt	0.34		6.84
	DEP2	1.25		6.08
	THI	1.94	43.34	5.01
	THP	-2.25		3.52
	DEP7	-0.30		1.45
	DEP1	0.44		1.23
	DEP4	0.49		1.14
	PTY	-0.88		0.99

The R-squared (R^2) values ranged between 0.196 (sulphate) and 0.563 (nitrate) with upto nine, but occasionally as few as three, predictor variables. Approximately 56% of the variation (R^2 of 0.563) in nitrate concentrations can be explained by the six catchment parameters selected by the stepwise method.

The full dataset of the water chemistry 'fluxes' (n = 55) were related to the 24 predictor variables (Table H11).

Table H11 – Stepwise regression analyses of the full 'flow-weighted' dataset (n=55)

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	7.444		-
	Annual Rainfall	-0.001		47.24
	SKS	-0.006	**75.07**	13.47
	Sea	0.012		8.51
	CLDEP6	-0.003		3.40
	Site Alt	-0.001		2.45
Sodium	Intercept	135.90		-
	BVG	-0.31	**23.51**	13.52
	GR	1.18		9.99
Magnesium	Intercept	106.10		-
	Annual Runoff	-0.02	**43.08**	35.77
	MIX	0.79		7.31
Calcium	Intercept	29.45		-
	AGR	1.67		50.09
	Sea	3.18	**67.87**	8.89
	FOR	1.04		5.92
	THP	1.36		2.97
Potassium	Intercept	2.13		-
	AGR	0.07	**55.18**	49.65
	THP	0.08		5.53
Chloride	Intercept	172.80		-
	Site Alt	-0.25		16.67
	CLDEP3	-0.36	**39.43**	8.76
	CLDEP1	-0.75		7.09
	THP	0.90		6.91
Nitrate	Intercept	-1.29		-
	AGR	0.27	**50.10**	39.89
	THP	1.34		5.22
	SKS	-0.51		4.99
Sulphate	Intercept	91.27		-
	BVG	-0.24	**24.50**	18.38
	FOR	0.40		6.12
Alkalinity	Intercept	217.26		-
	AGR	1.16		52.50
	Sea	3.34	**79.13**	16.28
	Annual Runoff	-0.108		7.76
	CLDEP7	1.15		2.59
Silica	Intercept	284.90		-
	Annual Runoff	-0.06	**49.37**	44.98
	CLDEP1	0.52		4.39

The R-squared (R^2) values ranged between 0.235 (sodium) and 0.791 (alkalinity) with upto five, but occasionally as few as two, predictor variables. Approximately 79% of the variation (R^2 of 0.791) in annual flow-weighted alkalinity can be explained by the four catchment parameters selected by the stepwise method.

The knowledge gleaned from Section 4.3 and the full '6 survey' and 'flow-weighted' stepwise regression models suggested that several agriculturally dominated catchments exert a large influence on the statistical analysis. Therefore, the agricultural sites were removed for the purpose of the subsequent statistical analysis.

H.1.3 Testing reduced models (i.e. agricultural sites removed)

The removal of the agricultural sites resulted in certain catchment categories having identical values (or empty columns) for every site (see Table H9 for details). The water chemistry concentrations from the reduced '6 survey' dataset (n = 264) were related to the 22 predictor variables (Table H12).

Table H12 – Stepwise regression analyses of the reduced '6 survey' dataset (n=264)

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	6.594		-
	Sea	0.024		15.18
	Discharge	-0.005		9.48
	SKS	-0.008	**37.44**	5.06
	DEP7	-0.004		4.40
	DEP2	0.004		2.16
	DEP6	-0.002		1.16
Sodium	Intercept	195.10		-
	BVG	-0.20		8.99
	Sea	-0.87	**21.67**	6.86
	GR	0.98		3.02
	UPL	-0.41		2.80
Magnesium	Intercept	84.65		-
	MIX	1.26	**24.10**	9.73
	Discharge	-0.42		8.14
	DEP7	-0.25		6.23
Calcium	Intercept	191.07		-
	Sea	4.22		18.78
	Max Alt	-0.06	**37.93**	12.69
	UPL	-0.99		2.61
	Discharge	-0.55		2.70
Potassium	Intercept	6.43		-
	Discharge	-0.04	**9.92**	5.06
	DEP7	-0.02		3.26
	MIX	0.09		1.60
Chloride	Intercept	169.70		-
	Site Alt	-0.05		16.31
	BVG	-0.33		7.40
	DEP6	-0.36	**35.21**	6.39
	GR	1.16		2.83
	FOR	0.48		2.28
Nitrate	Intercept	5.53		-
	FOR	0.36		16.36
	Max Alt	0.03		7.44
	SKS	-0.09	**36.32**	4.62
	Sea	0.34		2.10
	DEP5	-0.08		2.09
	DEP2	-0.10		2.08
	DEP4	-0.08		1.63
Sulphate	Intercept	127.00		-
	BVG	-0.45		15.62
	Discharge	-0.36	**28.89**	5.06
	DEP1	-0.54		3.04
	Max Alt	0.07		2.74
	UPL	-0.44		2.43
Alkalinity	Intercept	153.11		-
	DEP6	-0.07		18.20
	Max Alt	-0.16		8.38
	Sea	4.18		4.98
	MIX	2.82	**38.75**	2.32
	Discharge	-0.67		1.91
	THP	-2.08		1.54
	DEP7	-0.61		1.42
Silica	Intercept	228.78		-
	DEP2	1.19		12.08
	FOR	1.19		8.40
	Site Alt	0.21	**35.62**	6.11
	THI	1.90		3.26
	DEP7	-0.24		2.01
	THP	-3.23		1.92
	BVG	-0.62		1.04
	PTY	-0.87		0.80

The R-squared (R^2) values ranged between 0.099 (potassium) and 0.387 (alkalinity) with upto eight, but occasionally as few as three, predictor variables. Approximately 39% of the variation (R^2 of 0.387) in alkalinity concentrations can be explained by the six catchment parameters selected by the stepwise method.

The reduced 'flow-weighted' dataset of water chemistry 'fluxes' (n = 44) were related to the 23 predictor variables (Table H13).

Table H13 – Stepwise regression of the reduced 'flow-weighted' dataset (n=44)

Constituent	Stepwise Predictors	Parameter Estimate	R^2	Added explanation to total R^2 (%)
pH	Intercept	7.392		-
	Annual Rainfall	-0.001		32.87
	SKS	-0.006	**66.50**	19.95
	Sea	0.008		8.58
	CLDEP6	-0.003		5.40
Sodium	Intercept	140.40		-
	BVG	-0.34	**28.32**	16.53
	GR	1.11		11.81
Magnesium	Intercept	95.36		-
	Annual Runoff	-0.02	**41.28**	28.06
	MIX	0.85		13.22
Calcium	Intercept	136.65		-
	CLDEP2	0.46		36.63
	Sea	2.81	**70.67**	18.71
	Annual Runoff	-0.04		9.70
	FOR	0.76		5.63
Potassium	Intercept	6.89		-
	SIL	0.02		17.49
	Sea	-0.06	**33.18**	8.81
	Annual Runoff	-0.01		6.90
Chloride	Intercept	255.60		-
	Site Alt	-0.32		26.12
	CLDEP3	-0.45	**46.61**	11.85
	Annual Runoff	-0.03		8.64
Nitrate	Intercept	-8.17		-
	FOR	0.32	**43.12**	22.01
	Max Alt	0.03		13.85
	SKS	-0.11		7.26
Sulphate	Intercept	108.50		-
	BVG	-0.40	**27.39**	27.39
Alkalinity	Intercept	320.81		-
	Sea	3.03		36.67
	Annual Runoff	-0.14	**79.28**	26.22
	CLDEP7	1.60		9.47
	THP	-1.64		6.92
Silica	Intercept	243.40		-
	Annual Runoff	-0.05	**39.40**	33.18
	FOR	0.57		6.22

The R-squared (R^2) values ranged between 0.283 (sodium) and 0.793 (alkalinity) with upto four, but occasionally as few as one, predictor variables. Approximately 79% of the variation (R^2 of 0.793) in annual flow-weighted alkalinity can be explained by the four catchment parameters selected by the stepwise method.

Summary

The deposition load categories often appear together when the reduced datasets are used for statistical analysis. Despite their presence in the stepwise regression models, as already

identified in Chapter 4, they really don't reflect the effect of deposition alone. It is impossible to differentiate whether the deposition categories are actually a controlling factor in the water chemistry or whether they have been selected purely because they fit well (see Assumptions and potential problems in Section 2.5.1a). Therefore, to reduce confusion and help discriminate between actual and spurious patterns, the deposition loads determined by the 20 x 20km grid method and the Cl-balance method were discarded from the subsequent models. Nevertheless, in order to establish the role that deposition plays, the deposition categories were replaced by a single deposition variable (S&N Deposition). Each catchment was given a discrete value for its atmospheric deposition load of sulphur and nitrogen rather than a percentage areal coverage of the seven deposition categories. The load was calculated on a catchment-to-catchment basis using the Cl-balance method outlined in Section 4.2.2.

H.1.4 Testing regression assumptions

As identified in Section 2.5.1a, using percentages in multiple regression raises the problem of exact multicollinearity, but in this case the computer automatically eliminates any variables with high multicollinearity from the regression equation. By looking at the residuals and errors of the model, the other assumptions of regression modelling can be examined for the chemical constituents analysed in Section 5.2.2.

The residual is the observed value of the response variable minus the predicted value (i.e. actual data minus fitted data). Plotting the residual values of calcium against predicted calcium provides an indication of the distribution of variance. The assumption is that errors are independently distributed. A plot of residuals against the predicted value shows random scatter for all the variables (Figure H1 to H4). The lack of any systematic pattern suggests that the assumption was fulfilled in the case of the derived model.

A further assumption of the regression model is that error should exhibit a normal distribution. To assess the assumption of normal distribution studentized residuals are used. The 'deleted' residual is the residual for the i^{th} observation calculated with the i^{th} observation removed from the dataset. The studentized residual for the i^{th} observation is the 'deleted' residual divided by the standard deviation of the 'deleted' residual. The studentized residuals exhibit a normal distribution (Figures H1 to H4). The main assumptions of the regression model have been fulfilled.

Figure H1 - Plots of residuals versus predicted values and analysis of error distribution using studentized residuals for alkalinity.

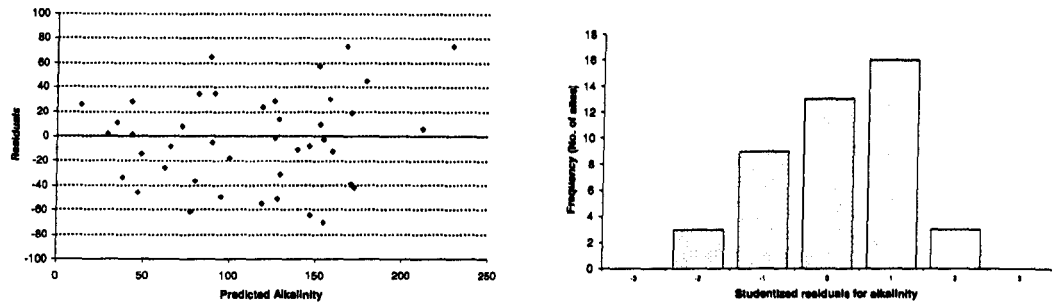


Figure H2 - Plots of residuals versus predicted values and analysis of error distribution using studentized residuals for calcium.

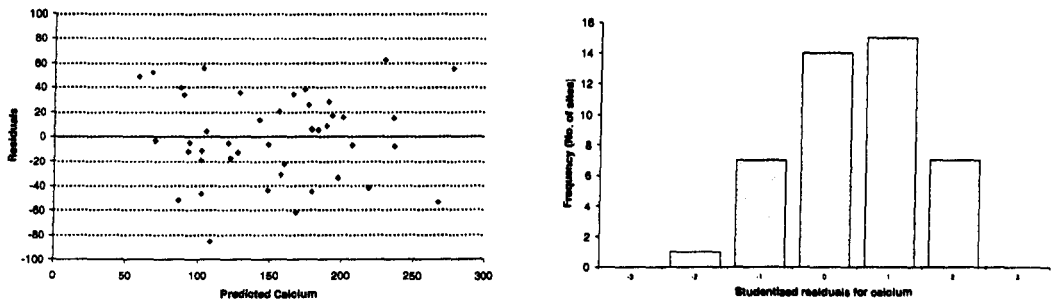


Figure H3 - Plots of residuals versus predicted values and analysis of error distribution using studentized residuals for pH.

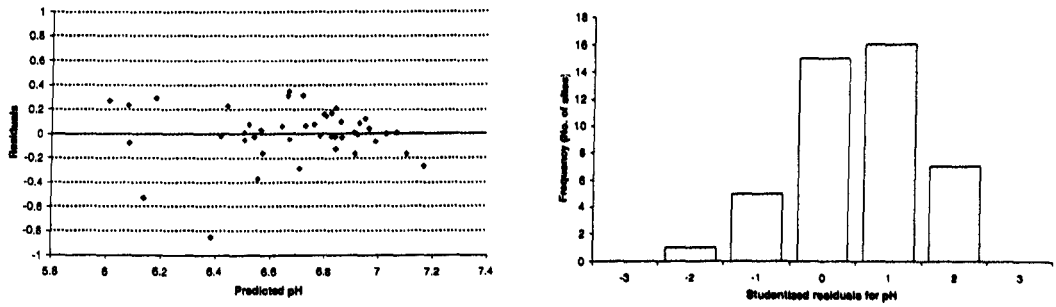
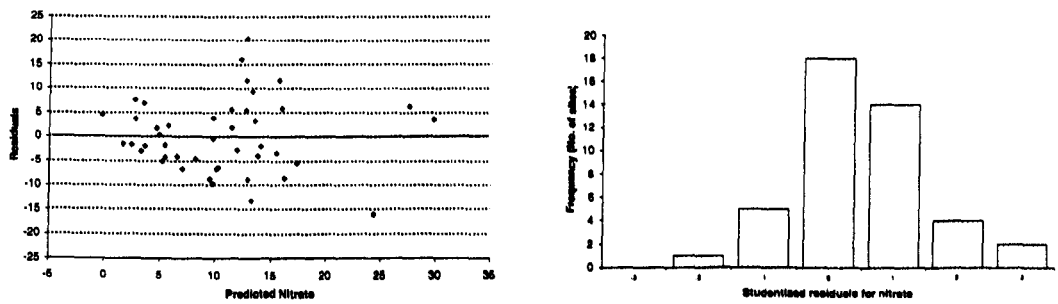


Figure H4 - Plots of residuals versus predicted values and analysis of error distribution using studentized residuals for nitrate.



H.2. Generation and testing of 'secondary' PCA models

PCA was carried out on the '6 survey' and 'flow-weighted' datasets to identify variables that behave similarly. The PCA results are interpreted by looking at i) the proportion of the variance associated with each principal component and ii) the correlation of the variables (i.e. loading) with each PCA axis. However, it is often easier to interpret the results by plotting the loadings of the PCA axes on a correlation biplot. The vectors on the correlation biplot point in the direction of maximum variation and their length is proportional to the variation. Bearing this in mind, arrowheads furthest from the origin are the most important indicators of site variation, whilst those nearest the origin are of less importance. Vectors which display acute angles are generally positively correlated and those with obtuse angles have negative correlations (TerBraak, 1983).

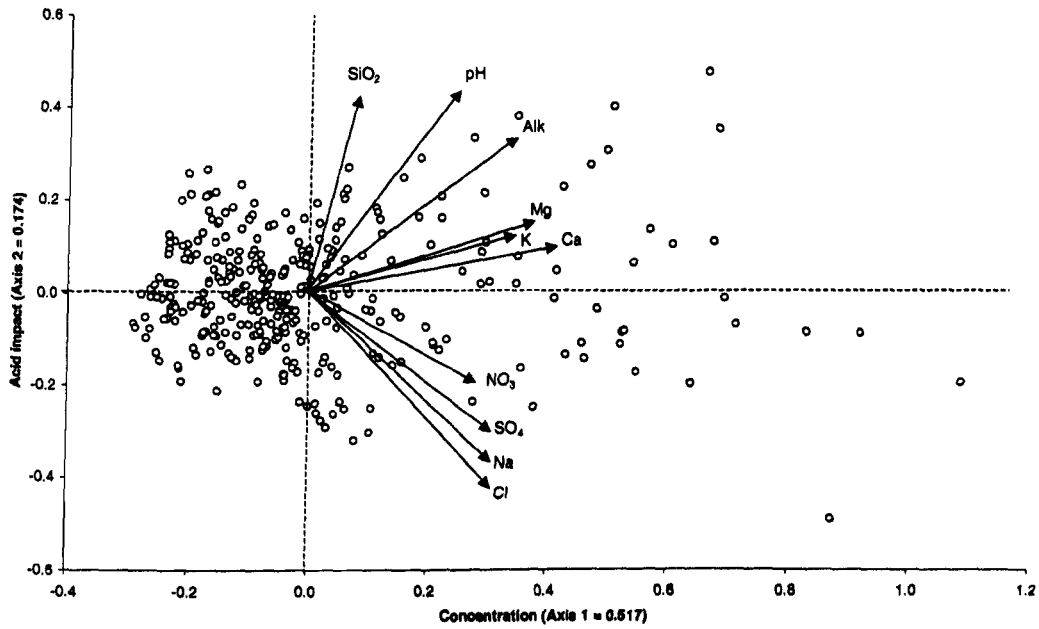
H.2.1 Testing '6 survey' datasets

In the first step, the full dataset of water chemistry concentrations were subjected to principal components analysis (Table H14). Approximately 52% of the variance associated with the water chemistry can be explained by the first PCA axis. The second axis is responsible for 17% of the variation, and axes 3 and 4 explain 9% and 8% respectively. It is important to note that the first four axes explain 86% of the total variation in the chemical data and more importantly the first two axes explain 69% of the chemical data's variation. The relationships in axis 1 show that the concentrations of the water chemistry variables are higher in some catchments than other catchments. Therefore, axis 1 is relatively unimportant to our interpretation. Axis 2 shows the highest positive correlations with pH (0.434), silica (0.423) and alkalinity (0.410), and the highest negative correlations with chloride (-0.438), sodium (-0.381) and sulphate (-0.309). The interpretation of these patterns becomes easier when they are presented on a correlation biplot (Figure H5).

Table H14 – Results of PCA on 10 water chemistry variables (n=330)

	PCA Axes 1	2	3	4
Eigenvalue	5.1696	1.7419	0.9058	0.7779
Proportion	0.517	0.174	0.091	0.078
Cumulative % variance	0.517	0.691	0.782	0.86
Variable loadings (correlations)				
pH	0.250	0.434	0.272	-0.361
Sodium	0.313	-0.381	0.068	0.463
Magnesium	0.381	0.155	0.222	0.270
Calcium	0.414	0.112	0.014	-0.063
Potassium	0.353	0.125	-0.193	-0.312
Chloride	0.309	-0.436	-0.205	0.112
Nitrate	0.282	-0.200	-0.429	-0.485
Sulphate	0.312	-0.309	0.162	-0.131
Alkalinity	0.345	0.331	0.236	0.262
Silica	0.081	0.423	-0.726	0.384

Figure H5 – Correlation biplot of 10 water chemistry variables (n=330)



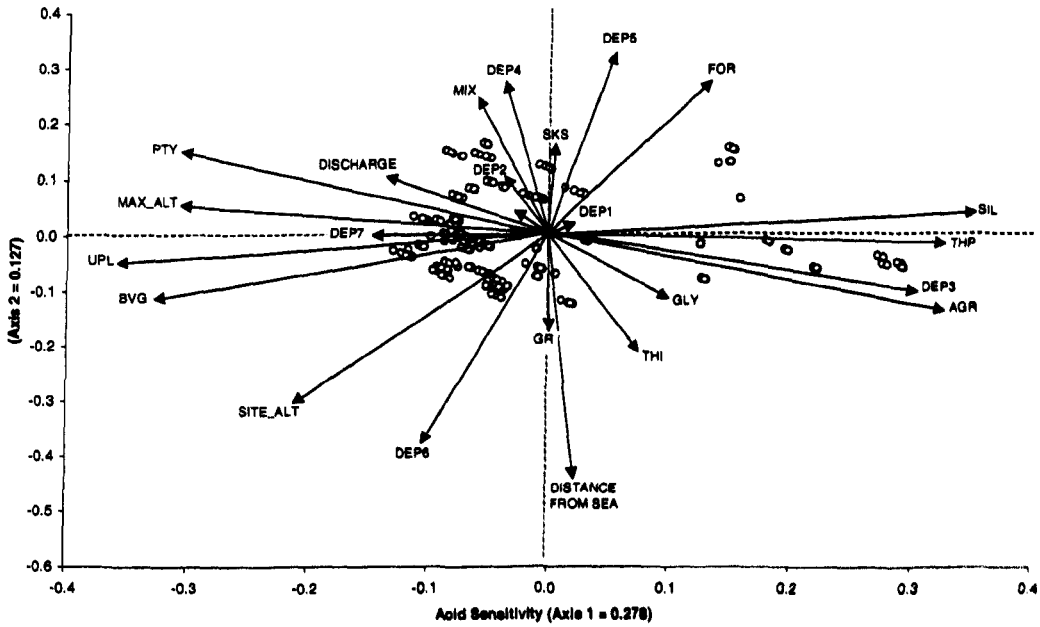
In the second step, PCA was used to examine the relationships among the 23 predictor variables of the full dataset (Table H15 and Figure H6). Approximately 28% of the variance can be explained by the first PCA axis. The second axis is responsible for 13% of the variation, and axes 3 and 4 explain 10% and 9% respectively. The first four axes explain 60% of the total variation in the data, of which the first two axes explain 40%. Axis 1 shows the highest positive correlations with SIL (0.357), AGR (0.334), THP (0.331) and DEP3 (0.308), and the highest negative correlations with UPL (-0.356), BVG (-0.324), PTY

(-0.307) and Maximum altitude (-0.305). Axis 2 shows the highest positive correlations with DEP5 (0.330), DEP4 (0.272) and FOR (0.267) and the highest negative correlations with Distance from the sea (-0.461), DEP6 (-0.391) and Site altitude (-0.315).

Table H15 – Results of PCA on 23 catchment characteristic variables (n=330)

	PCA Axes			
	1	2	3	4
Eigenvalue	6.387	2.9144	2.3421	2.1245
Proportion	0.278	0.127	0.102	0.092
Cumulative % variance	0.278	0.404	0.506	0.599
Variable loadings (correlations)				
BVG	-0.324	-0.121	0.108	0.26
SKS	0.008	0.157	-0.433	-0.32
SIL	0.357	0.021	0.159	-0.08
MIX	0.008	-0.183	0.043	-0.261
GR	-0.06	0.238	-0.163	0.144
UPL	-0.356	-0.058	-0.182	-0.003
FOR	0.135	0.267	0.397	-0.105
AGR	0.334	-0.127	-0.069	0.082
THP	0.331	-0.026	-0.242	-0.001
THI	0.078	-0.227	-0.122	0.476
GLY	0.102	-0.12	-0.111	-0.153
PTY	-0.307	0.148	0.262	-0.134
DEP1	0.007	0.042	-0.27	-0.308
DEP2	-0.037	0.134	-0.123	-0.155
DEP3	0.308	-0.114	-0.116	0.131
DEP4	-0.039	0.272	-0.292	0.049
DEP5	0.06	0.33	0.365	-0.088
DEP6	-0.1	-0.391	0.091	-0.238
DEP7	-0.142	-0.01	0.014	0.417
Q	-0.134	0.096	-0.147	-0.031
SITE_ALT	-0.21	-0.315	0.058	-0.241
MAX_ALT	-0.305	0.046	-0.195	0.013
SEA	0.025	-0.461	0.079	-0.112

Figure H6 – Correlation biplot of 23 catchment characteristic variables (n=330)

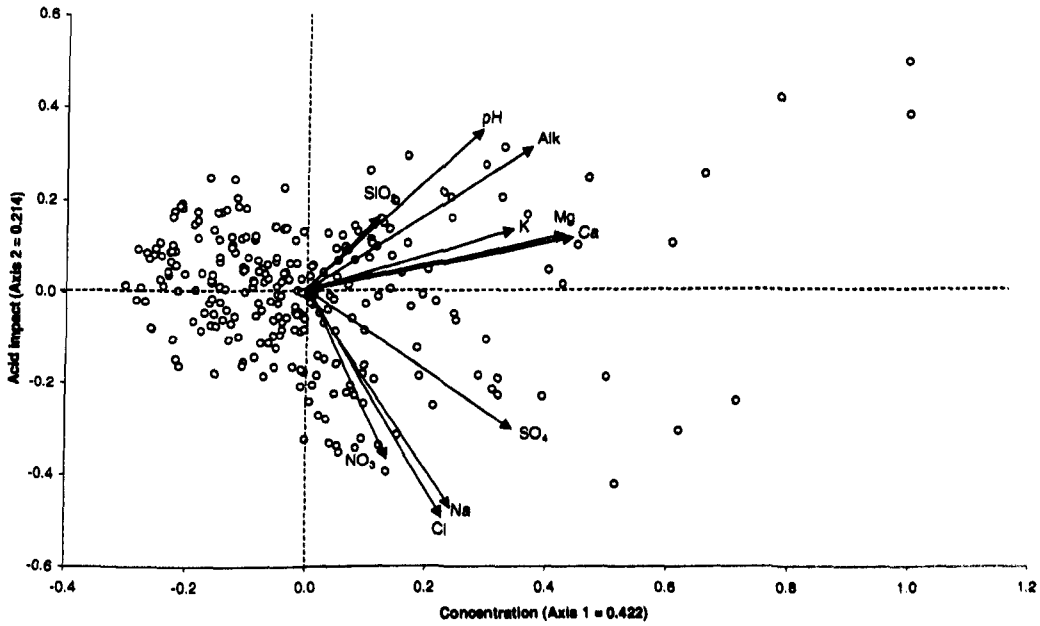


In the third step, the reduced dataset of water chemistry concentrations were subjected to principal components analysis (Table H16 and Figure H7). Approximately 42% of the variance associated with the water chemistry can be explained by the first PCA axis. The second axis is responsible for 21% of the variation, and axes 3 and 4 explain 11% and 9% respectively. The first four axes explain 83% of the total variation in the chemical data, of which the first two axes explain 64%. Again the correlations in the first axis represent the variation in the water chemistry concentrations. Axis 2 shows the highest positive correlations with pH (0.347) and alkalinity (0.306), and the highest negative correlations with chloride (-0.503), sodium (-0.481), nitrate (-0.368) and sulphate (-0.304).

Table H16 – Results of PCA on 10 water chemistry variables (without agricultural sites. n=264)

	PCA Axes			
	1	2	3	4
Eigenvalue	4.216	2.1403	1.0603	0.861
Proportion	0.422	0.214	0.106	0.086
Cumulative % variance	0.422	0.636	0.742	0.828
Variable loadings (correlations)				
pH	0.289	0.347	0.33	0.111
Sodium	0.245	-0.481	-0.208	-0.395
Magnesium	0.433	0.121	-0.083	-0.199
Calcium	0.443	0.115	0.057	-0.037
Potassium	0.353	0.139	0.014	0.371
Chloride	0.231	-0.503	-0.246	0.022
Nitrate	0.133	-0.368	0.388	0.564
Sulphate	0.345	-0.304	0.203	0.046
Alkalinity	0.378	0.306	-0.025	-0.317
Silica	0.124	0.163	-0.765	0.482

Figure H7 – Correlation biplot of 10 water chemistry variables (n=330)

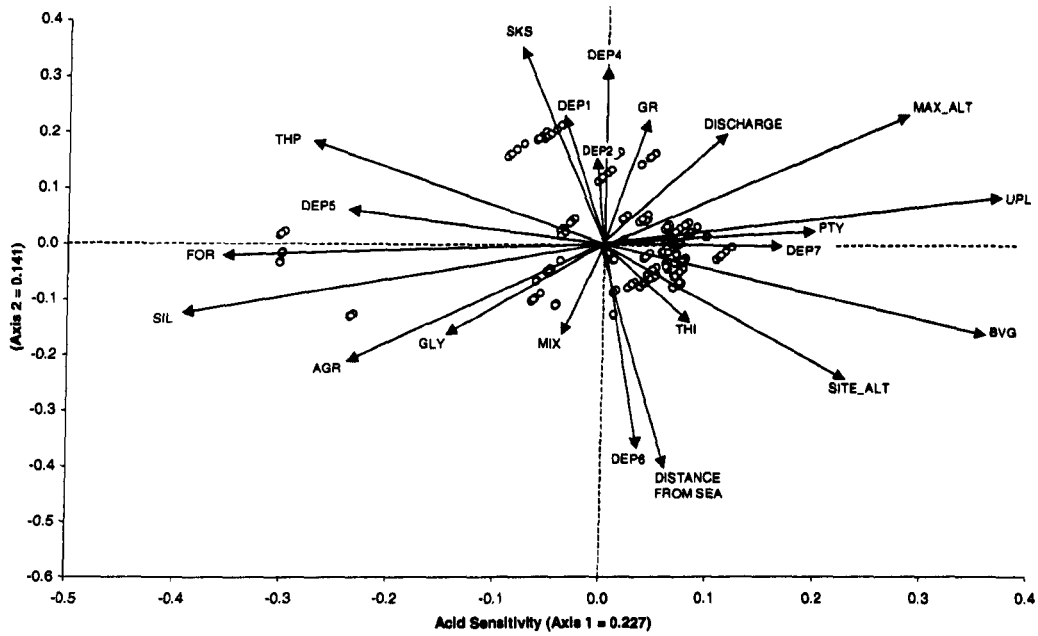


In the fourth step, PCA was used to examine the relationships among the 22 predictor variables of the 'reduced' dataset (Table H17 and Figure H8). Approximately 23% of the variance can be explained by the first PCA axis. The second axis is responsible for 14% of the variation, and axes 3 and 4 explain 13% and 10% respectively. The first four axes explain 60% of the total variation in the data, of which the first two axes explain 37%. Axis 1 shows the highest negative correlations with SIL (-0.394), FOR (-0.357) and THP (-0.277), and the highest positive correlations with UPL (0.379), BVG (0.360) and Maximum altitude (0.287). Axis 2 shows the highest positive correlations with SKS (0.355), DEP4 (0.326) and GR (0.236) and the highest negative correlations with Distance from the sea (-0.394) and DEP6 (-0.377).

Table H17 – Results of PCA on 22 catchment characteristic variables
(without agricultural sites. n=264)

	PCA Axes			
	1	2	3	4
Eigenvalue	4.9831	3.1044	2.8787	2.1852
Proportion	0.227	0.141	0.131	0.099
Cumulative % variance	0.227	0.368	0.498	0.598
Variable loadings (correlations)				
BVG	0.36	-0.155	0.224	0.146
SKS	-0.077	0.355	-0.36	-0.061
SIL	-0.394	-0.126	0.039	-0.097
MIX	-0.037	-0.155	-0.205	-0.258
GR	0.03	0.236	0.074	0.102
UPL	0.379	0.059	-0.239	0.041
FOR	-0.357	-0.021	0.259	-0.067
AGR	-0.235	-0.211	-0.032	0.112
THP	-0.277	0.18	-0.369	0.055
THI	0.081	-0.126	-0.067	0.533
GLY	-0.147	-0.171	-0.203	0.248
PTY	0.2	0.024	0.359	-0.413
DEP1	-0.033	0.215	-0.251	-0.105
DEP2	-0.003	0.163	-0.056	-0.106
DEP4	-0.002	0.326	-0.03	0.069
DEP5	-0.231	0.07	0.305	-0.144
DEP6	0.033	-0.377	-0.27	-0.176
DEP7	0.171	-0.007	0.149	0.352
Q	0.118	0.19	-0.029	-0.194
SITE_ALT	0.227	-0.24	-0.179	-0.304
MAX_ALT	0.287	0.229	-0.084	-0.079
SEA	0.061	-0.394	-0.199	-0.108

Figure H8 – Correlation biplot of 22 catchment characteristic variables (n=264)



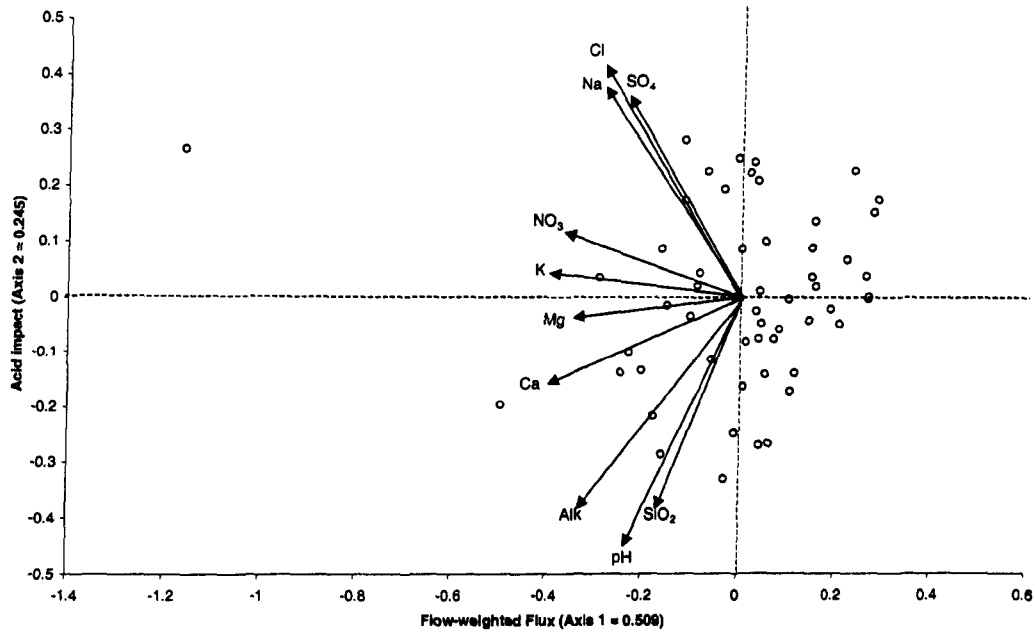
H.2.2 Testing 'flow-weighted' datasets

Approximately 51% of the variance associated with the water chemistry concentrations from the full dataset can be explained by the first PCA axis (Table H18 and Figure H9). The second axis is responsible for 25% of the variation, and axes 3 and 4 explain 8% and 6%. The first four axes explain 89% of the total variation in the chemical data, of which the first two axes explain 75%. The correlations in the first axis represent the variation in the water chemistry and are relatively unimportant to our interpretation. Axis 2 shows the highest positive correlations with chloride (0.410), sodium (0.391) and sulphate (0.365) and the highest negative correlations with pH (-0.451), alkalinity (-0.389) and silica (-0.383).

Table H18 – Results of PCA on 10 water chemistry variables (n=55)

	PCA Axes			
	1	2	3	4
Eigenvalue	5.0894	2.4483	0.7777	0.5583
Proportion	0.509	0.245	0.078	0.056
Cumulative % variance	0.509	0.754	0.832	0.887
Variable loadings (correlations)				
fw_pH	-0.226	-0.451	-0.032	-0.472
fw_na	-0.272	0.391	-0.409	0.178
fw_mg	-0.355	-0.04	-0.353	0.365
fw_ca	-0.406	-0.163	0.22	-0.178
fw_k	-0.398	0.049	0.24	0.333
fw_cl	-0.285	0.41	-0.127	-0.197
fw_no3	-0.367	0.118	0.492	0.189
fw_so4	-0.258	0.365	-0.074	-0.626
fw_alk	-0.333	-0.389	0.108	0.031
fw_si	-0.179	-0.383	-0.57	0.039

Figure H9 – Correlation biplot of 10 water chemistry variables (n=55)

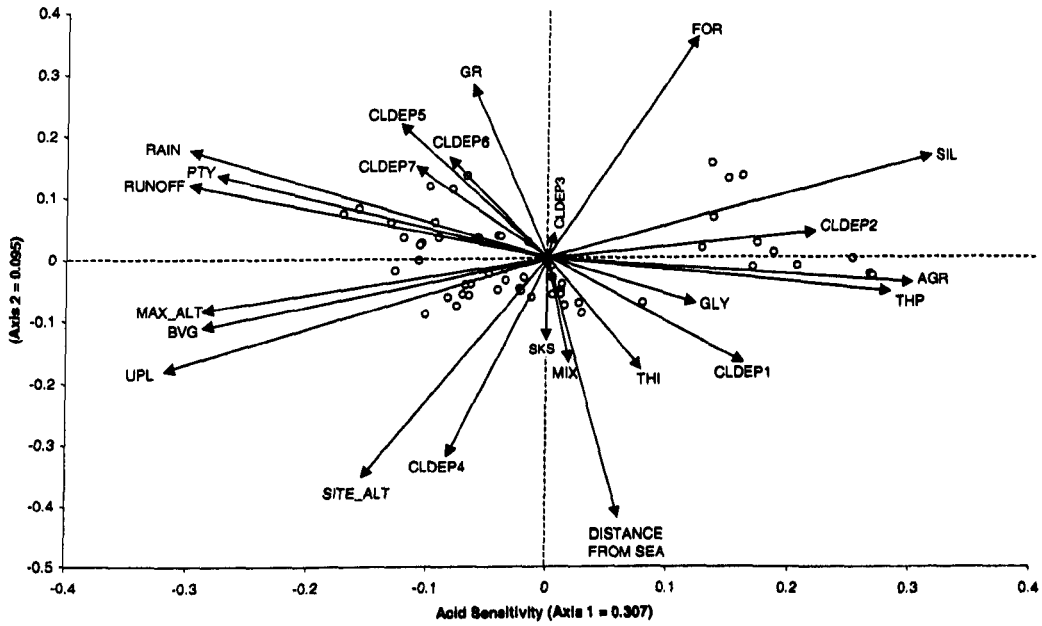


Approximately 31% of the variance associated with the 24 predictor variables from the full dataset can be explained by the first PCA axis (Table H19). The second axis is responsible for 10% of the variation, and axes 3 and 4 explain 9% and 8% respectively. The first four axes explain 57% of the total variation in the data, of which the first two axes explain 40%. Axis 1 shows the highest positive correlations with SIL (0.320), AGR (0.303) and THP (0.286) and the highest negative correlations with UPL (-0.323), Annual rainfall (-0.306), Annual runoff (-0.302), Maximum altitude (-0.299), BVG (-0.288) and PTY (-0.281). Axis 2 shows the highest positive correlations with FOR (0.360) and GR (0.279) and the highest negative correlations with Distance from the sea (-0.458), Site altitude (-0.367) and CLDEP4 (-0.313). These patterns are presented on a correlation biplot (Figure H10).

Table H19– Results of PCA on 24 catchment characteristic variables (n=55)

	PCA Axes			
	1	2	3	4
Eigenvalue	7.3797	2.2912	2.1339	1.8828
Proportion	0.307	0.095	0.089	0.078
Cumulative % variance	0.307	0.403	0.492	0.57
Variable loadings (correlations)				
BVG	-0.288	-0.113	0.115	0.327
SKS	0.002	-0.142	-0.339	-0.483
SIL	0.32	0.166	0.058	-0.075
MIX	0.019	-0.152	0.202	-0.112
GR	-0.065	0.279	-0.13	0.081
UPL	-0.323	-0.182	-0.017	-0.032
FOR	0.122	0.36	0.19	-0.191
AGR	0.303	-0.043	-0.117	0.177
THP	0.286	-0.054	-0.324	-0.091
THI	0.077	-0.177	-0.226	0.484
GLY	0.124	-0.075	0.032	0
PTY	-0.281	0.133	0.312	-0.121
CLDEP1	0.148	-0.162	-0.176	0.23
CLDEP2	0.22	0.045	0.161	-0.035
CLDEP3	0.002	0.025	0.314	0.108
CLDEP4	-0.089	-0.313	-0.207	-0.39
CLDEP5	-0.123	0.211	0.034	0.051
CLDEP6	-0.088	0.169	-0.071	0.029
CLDEP7	-0.114	0.148	-0.265	0.217
RAIN	-0.306	0.159	-0.192	0.038
RUNOFF	-0.302	0.13	-0.214	0.074
SITE_ALT	-0.156	-0.367	0.304	-0.053
MAX_ALT	-0.299	-0.091	-0.192	-0.095
SEA	0.066	-0.458	0.138	0.149

Figure H10 – Correlation biplot of 24 catchment characteristic variables (n=55)



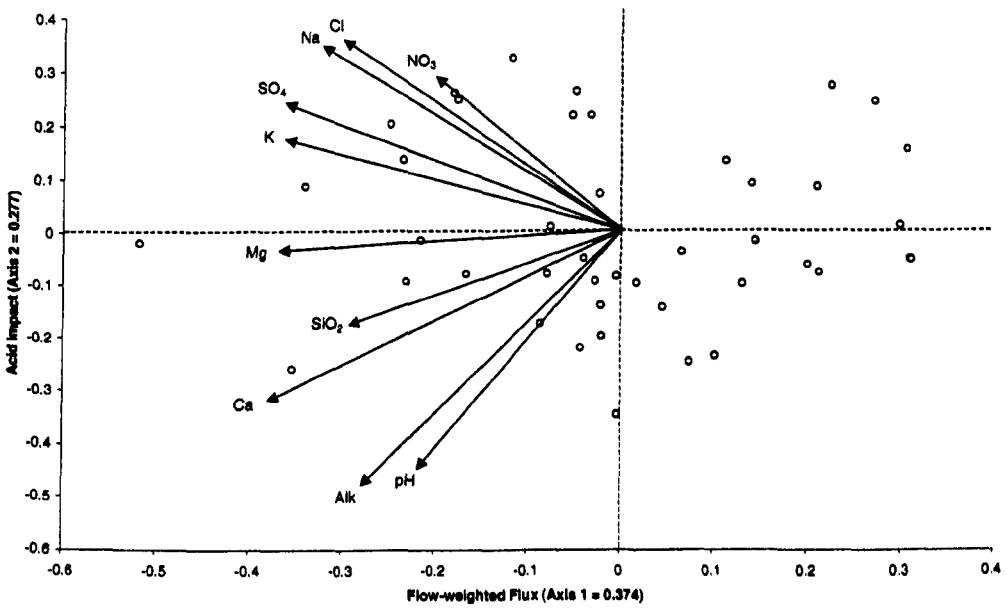
Approximately 37% of the variance associated with the water chemistry concentrations from the 'reduced' dataset can be explained by the first PCA axis (Table H20 and Figure H11). The second axis is responsible for 28% of the variation, and axes 3 and 4 explain 10% and 7% respectively. The first four axes explain 83% of the total

variation in the chemical data, of which the first two axes explain 65%. Again the correlations in the first axis represent the variation in the water chemistry and are relatively unimportant to our interpretation. Axis 2 shows the highest positive correlations with chloride (0.355), sodium (0.345) and nitrate (0.289) and the highest negative correlations with alkalinity (-0.484), pH (-0.456) and calcium (-0.323). Axis 3 shows the highest positive correlations with magnesium (0.605) and the highest negative correlations with nitrate (-0.570). Axis 4 shows the highest positive correlations with sulphate (0.378) and the highest negative correlations with silica (-0.834).

Table H20 - Results of PCA on 10 water chemistry variables (n=44)

	PCA Axes			
	1	2	3	4
Eigenvalue	3.7423	2.7723	1.0416	0.7336
Proportion	0.374	0.277	0.104	0.073
Cumulative % variance	0.374	0.651	0.756	0.829
Variable loadings (correlations)				
fw_pH	-0.221	-0.456	-0.153	0.208
fw_na	-0.324	0.345	0.275	0.011
fw_mg	-0.371	-0.035	0.605	0.101
fw_ca	-0.382	-0.323	-0.211	0.283
fw_k	-0.366	0.172	0.256	-0.142
fw_cl	-0.3	0.355	-0.192	-0.059
fw_no3	-0.204	0.289	-0.57	-0.068
fw_so4	-0.363	0.24	-0.22	0.378
fw_alk	-0.276	-0.484	-0.016	-0.005
fw_si	-0.297	-0.189	-0.116	-0.834

Figure H11 – Correlation biplot of 10 water chemistry variables (n=44)

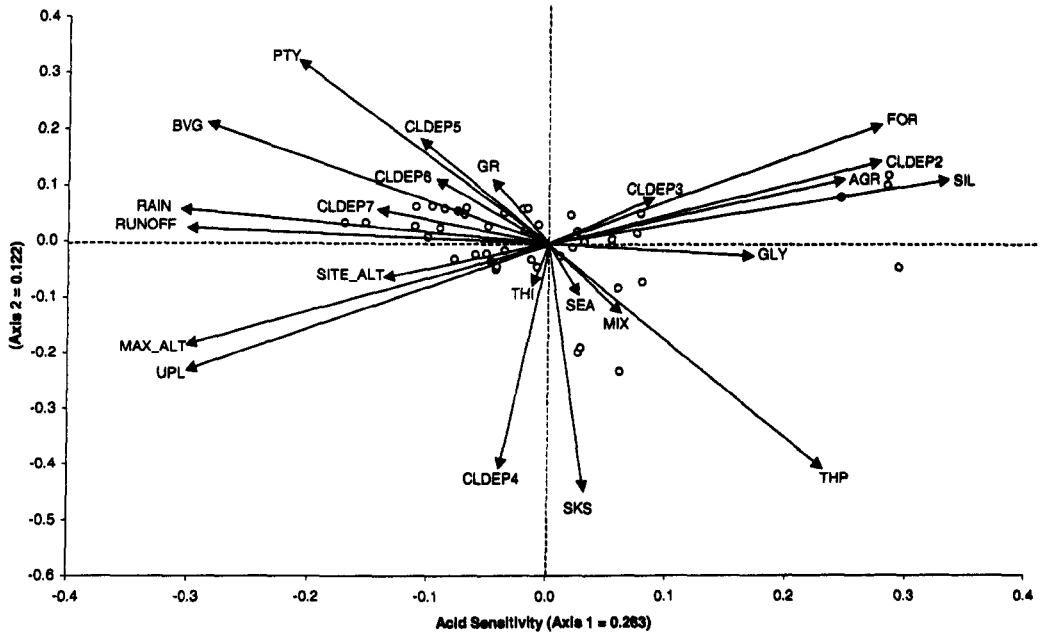


Approximately 26% of the variance associated with the 23 predictor variables from the 'reduced' dataset can be explained by the first PCA axis (Table H21 and Figure H12). The second axis is responsible for 12% of the variation, and axes 3 and 4 explain 11% and 9% respectively. The first four axes explain 58% of the total variation in the data, of which the first two axes explain 38%. Axis 1 shows the highest positive correlations with SIL (0.336), FOR (0.278) and CLDEP2 (0.274) and the highest negative correlations with Annual rainfall (-0.315), UPL (-0.307), Annual runoff (-0.305), Maximum altitude (-0.303) and BVG (-0.289). Axis 2 shows the highest positive correlations with PTY (0.324) and FOR (0.224) and the highest negative correlations with SKS (-0.466), THP (-0.421) and CLDEP4 (-0.414).

Table H21 - Results of PCA on 23 catchment characteristic variables (n=44)

	PCA Axes			
	1	2	3	4
Eigenvalue	6.0465	2.7966	2.5639	2.018
Proportion	0.263	0.122	0.111	0.088
Cumulative % variance	0.263	0.384	0.496	0.584
Variable loadings (correlations)				
BVG	-0.289	0.211	0.272	-0.15
SKS	0.04	-0.466	-0.241	0.101
SIL	0.336	0.104	-0.13	0.084
MIX	0.053	-0.11	0.163	0.247
GR	-0.049	0.099	-0.197	-0.137
UPL	-0.307	-0.234	0.202	-0.12
FOR	0.278	0.224	-0.231	0.178
AGR	0.248	0.112	0.091	-0.241
THP	0.23	-0.421	-0.202	-0.014
THI	-0.018	-0.077	0.208	-0.469
GLY	0.174	-0.034	0.087	-0.398
PTY	-0.214	0.324	-0.014	0.421
CLDEP2	0.274	0.139	0.03	-0.154
CLDEP3	0.086	0.078	0.26	0.04
CLDEP4	-0.04	-0.414	0.02	0.168
CLDEP5	-0.119	0.181	-0.097	0.079
CLDEP6	-0.096	0.106	-0.146	-0.017
CLDEP7	-0.147	0.055	-0.239	-0.287
RAIN	-0.315	0.049	-0.274	-0.078
RUNOFF	-0.305	0.026	-0.248	-0.161
SITE_ALT	-0.142	-0.078	0.372	0.209
MAX_ALT	-0.303	-0.189	-0.134	0.008
SEA	0.026	-0.1	0.376	0.054

Figure H12 – Correlation biplot of 23 catchment characteristic variables (n=44)



<u>Summary</u>

The deposition load variables, DEP and CLDEP, don't really reflect the effect of deposition alone despite their presence in some of the PCA models. However, as described earlier in Chapter 5, the deposition loads were discarded and replaced by a single deposition variable, S&N Deposition, for the 'best' models (Section 5.2.3).